

NATIONAL GROUND WATER ASSOCIATION

Presents

**The Southwest Focused Ground Water Conference:
Discussing the Issue of MTBE and Perchlorate in
Ground Water**

Co-sponsors:

**American Petroleum Institute
California Groundwater Association
Association of California Water Agencies
Groundwater Resource Association of California
Western States Petroleum Association**



**June 3-4, 1998
Anaheim, California**

SCHEDULE

WEDNESDAY, JUNE 3, 1998

7:00 a.m. – 4:00 p.m. Registration

Presentation of Papers (*Medallion II & III*)

Moderator Tom Johnson, Levine • Frike • Recon

**8:15 a.m. – 8:45 a.m. California Water – Is It Safe?
Walt Pettit, California Water Resources Control Board
(keynote speaker)**

**8:45 a.m. – 9:10 a.m. Oxygenate Use in Gasoline – When, What and Why—
Lewis M. Gibbs**

**9:10 a.m. – 9:35 a.m. Getting Reliable Data From Water Labs Testing for MTBE
(or any other Volatile Contaminant—Bill Draper**

**9:35 a.m. – 10:00 a.m. Evaluation of EPA & ASTM Methods for Analysis of
Oxygenates in Gasoline Contaminated Groundwater—Rolf
U. Halden, Sarah R. Schoen, Yakov Galperin, Issac R. Kaplan,
Anne M. Happel**

**10:00 a.m. – 10:15 a.m. REFRESHMENT BREAK
Hosted by Levine • Frike • Recon**

**10:15 a.m. – 10:40 a.m. Occurrence and Behavior of MTBE in Ground Water—
Timothy E. Buscheck, Dan J. Gallagher, Tom R. Peargin,
Donald L. Kuehne, Charles R. Zuspan**

**10:40 a.m. – 11:05 a.m. Environmental Behavior and Fate of Methyl Tertiary Butyl
Ether (MTBE)—Paul J. Squillace, James F. Pankow, John S.
Zogorski**

**11:05 a.m. – 11:30 a.m. Fate and Transport of MTBE in Groundwater – Results of
a Controlled Field Experiment in Light of Other
Experience—James F. Barker, Mario Schirmer, Barbara J.
Butler, Clinton D. Church**

11:30 a.m. – 12:30 p.m. LUNCH (on your own)

Moderator Seena Hoose, Santa Clara Water District

**12:30 p.m. – 12:55 p.m. Methyl Tertiary Butyl Ether Plume Evolution at California
LUFT Sites—Edwin H. Beckenbach, Anne M. Happel**

WEDNESDAY, JUNE 3, 1998 (continued)

- 12:55 p.m. – 1:20 p.m. **Methyl Tertiary Butyl Ether (MTBE) Contamination of the City of Santa Monica Drinking Water Supply – An Update**—Anthony Brown, J.R.C. Farrow, R.A. Rodriguez, B.J. Johnson
- 1:20 p.m. – 1:45 p.m. **Santa Clara Valley Water District's Leaking UST Oversight Program "MTBE Issues in Santa Clara County Ground Water Supplies"**—James S. Crowley, Chris Tulloch
- 1:45 p.m. – 2:10 p.m. **Comparison of Alternative Technologies for Remediation of MTBE in Soil, Ground Water, and Surface**—Michael Kavanaugh
- 2:10 p.m. – 2:35 p.m. **Mechanism and Efficiency of the Degradation of MTBE in Contaminated Groundwater by the UV/H₂O₂ Process**—James R. Bolton, Ali Safarzadeh-Amiri, Stephen R. Carter, Bertrand Dussert, Mihaela I. Stefan, John Mack
- 2:35 p.m. – 2:50 p.m. **REFRESHMENT BREAK**
- 2:50 p.m. – 3:15 p.m. **Perspectives on MTBE Biodegradation and the Potential for In Situ Aquifer Bioremediation**—Joseph P. Salanitro, Chi-Su Chou, Halina L. Wisniewski & Timothy E. Vipond
- 3:15 p.m. – 3:40 p.m. **MTBE Biodegradation in the Presence of Other Gasoline Components**—Juana B. Eweis, Naoko Watanabe, Edward D. Schroeder, Daniel P.Y. Chang, Kate M. Schow
- 3:40 p.m. – 4:05 p.m. **Important Ecological Risk Assessment Parameters for MTBE and Other Gasoline Oxygenates**—Eugene R. Mancini, W.A. Stubblefield, H. Tillquist
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- 4:30 p.m. – 4:55 p.m. **Public Health Implications of MTBE and Perchlorate In Water: Risk Management Decisions for Water Purveyors**—James J.J. Clark, A. Brown, R.A. Rodriguez, B.J. Johnson
- 4:55 p.m. – 5:20 p.m. **A Basin Protection Strategy for Sites with MTBE Impacts**—Kevin L. Graves, N. Scott MacLeod
- 5:20 p.m. – 5:45 p.m. **MTBE – The Need for A Balanced Perspective**—Curtis C. Stanley

Conference Adjourns for the Day

THURSDAY, JUNE 4, 1998

7:30 a.m. – 2:00 p.m. Registration

Presentation of Papers (*Medallion II & III*)

Moderator	Kevin Mayer, U.S. EPA
8:15 a.m. – 8:40 a.m.	Growing Regulatory Awareness of MTBE & Perchlorate—Ken Williams
8:40 a.m. – 9:05 a.m.	Potential Claims for Water Purveyors Impacted by MTBE or Perchlorate—Gregory J. Patterson
9:05 a.m. – 9:30 a.m.	Perchlorate – A True Partnering Initiative—Major Dan Rogers
9:30 a.m. – 9:55 a.m.	The Analysis for Perchlorate by Ion Chromatography: The California DHS Method—H.S. Okamoto, D.K. Rishi, S.K. Perera
9:55 a.m. – 10:10 a.m.	REFRESHMENT BREAK
10:10 a.m. – 10:35 a.m.	Perchlorate in Lake Mead—Kay Brothers
10:35 a.m. – 11:00 a.m.	Dealing with Perchlorate Contamination in the San Gabriel Valley—Carol Williams
11:00 a.m. – 11:25 a.m.	Biodegradation of Perchlorate in Ground Water—Michael Girard
11:25 a.m. – 11:50 a.m.	The Biological Reduction of Perchlorate at Low Concentrations in Water – Technology Application in San Gabriel Basin, California—John G. Catts
11:50 a.m. – 1:20 p.m.	LUNCH PROVIDED Senator Richard Mountjoy (speaker)
Moderator	Jim Goodrich, San Gabriel Basin Water Quality Authority
1:20 p.m. – 1:45 p.m.	Air Force Perchlorate Technology Program—Jim Hurley
1:45 p.m. – 2:10 p.m.	Application of Ion Exchange Process for Perchlorate Removal—Issam Najm
2:10 p.m. – 2:35 p.m.	Microbiological Treatment of Perchlorate Contaminated Ground Waters—Bruce E. Logan, Kijung Kim

THURSDAY, JUNE 4, 1998 (continued)

- 2:35 p.m. – 3:00 p.m. **Microbial Conversion of Perchlorate, Chlorate and Chlorite**—CG van Ginkel, AGM Kroon, GB Rikken, SWM Kengen
- 3:00 p.m. – 3:25 p.m. **Treatment of Low Concentrations of Perchlorate, Status and Ongoing Research**—Frank Blaha
- 3:25 p.m. – 3:40 p.m. **REFRESHMENT BREAK**
- 3:40 p.m. – 4:05 p.m. **Human Health Risk Assessment of Perchlorate**—Joan Dollarhide
- 4:05 p.m. – 4:30 p.m. **Exposure Concerns and Health Implications of Perchlorate**—Marilyn Underwood
- 4:30 p.m. – 4:55 p.m. **Public Health Goals for California Drinking Water: Methyl Tertiary Butyl Ether (MTBE) and Perchlorate**—Joseph P. Brown
- 4:55 p.m. – 5:20 p.m. **MTBE and Perchlorate in Drinking Water: Regulatory and Policy Issues**—Michael Osinski

Proceedings of the Southwest Focused
Ground Water Conference
June 3-4, 1998
Anaheim, California

The 1998 Southwest Focused Ground Water Conference is sponsored by the National Ground Water Association. The Conference is co-sponsored by the following organizations:

- American Petroleum Institute;
- California Groundwater Association;
- Association of California Water Agencies;
- Groundwater Resource Association of California;
- Western States Petroleum Association.

This spiral bound volume is a compilation of papers that were submitted for publication and presented at the conference. Not all papers presented were submitted for publication.

The focused topics of MTBE and Perchlorate in ground water and surface water was selected due to the presence and potential impacts of these compounds in ground water and surface water of the Southwestern United States. These two compounds

- Appear to be recalcitrant in the environment;
- Have advisory levels, but no health or environment based regulatory levels;
- May have issues with laboratory analysis;
- Have a range of unproven remediation techniques; and
- Have impacted water supplies in some areas.

The conference is designed to provide state-of-the-art information about these two compounds. Conclusions drawn by the various authors may change based on future research and/or applications. The conference is also designed to bring together researchers, regulators, and water users to discuss the relative pertinent issues.

Responsibility: The National Ground Water Association nor its' co-sponsors are not responsible for statements and opinions advanced in the conference or printed publications.

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Evaluation of EPA and ASTM Methods for Analysis of Oxygenates in Gasoline-Contaminated Ground Water

Rolf U. Halden,¹ Sarah R. Schoen,² Yakov Galperin,³ Issac R. Kaplan,⁴ and
Anne M. Happel⁵

The recent use of oxygenates in reformulated gasoline necessitates the development and evaluation of analytical methods suitable for monitoring these compounds in ground water in the presence of gasoline interferences. Candidate analytical methods routinely performed in both research and commercial laboratories include modified versions of EPA Method 8020/8021 (GC-PID), EPA Method 8260 (GC-MS), and ASTM Method D4815 (two-dimensional GC/FID). An inter-laboratory study was initiated to determine practical quantification limits (PQLs), method detection limits (MDLs), and linear ranges for methyl *teritary*-butyl ether (MTBE), ethyl *teritary*-butyl ether (ETBE), diisopropyl ether (DIPE), *teritary*-amyl methyl ether (TAME) and *teritary*-butyl alcohol (TBA). In addition, a series of spiked matrices are being analyzed (water samples with dissolved gasoline at 0.5, and 50 ppm containing ethers at 35 ppb and TBA at 500 ppb; neat gasoline containing each oxygenate at 2000 ppm) to determine the accuracy, precision and robustness of the methods. Results of this study will show the potential and limitations of each of the methods for detecting and quantifying fuel oxygenates in environmental samples from leaking underground fuel tank (LUFT) sites.

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OCCURRENCE AND BEHAVIOR OF MTBE IN GROUNDWATER

Timothy E. Buscheck, Dan J. Gallagher, Tom R. Peargin, Donald L. Kuehne, and Charles R. Zuspan - Chevron Research and Technology Company

ABSTRACT

Empirical databases or multi-site "plume studies" have contributed to our understanding of the fate and transport of petroleum hydrocarbons dissolved in groundwater. Plume studies conducted by Lawrence Livermore National Laboratory (Rice et al. 1995) and the University of Texas, Bureau of Economic Geology (Mace et al. 1997) have examined the behavior of benzene in groundwater plumes. Similar plume studies, which include interpretation of methyl tertiary-butyl ether (MTBE) analytical data, will improve our understanding of this chemical.

To conduct this study, the authors examined groundwater analytical data for more than 700 service station sites nationwide where groundwater was analyzed for MTBE. MTBE was detected at approximately 80% of the investigated sites. MTBE was detected at 88% of operating sites, and at 74% of non-operating sites. The frequency of MTBE occurrence at non-operating sites is less than that at operating sites, because some of the service stations were closed prior to its use in gasoline. The detection frequency at operating sites in California (83%) is slightly less than in Texas (96%) and Maryland (98%). Later introduction of MTBE in California, coupled with early facility upgrades, required by the 1998 regulations, may contribute to the lower detection frequency in this state. Maximum MTBE concentrations also vary across the country, due to hydrogeologic conditions and the timing of MTBE introduction and composition in gasoline. MTBE concentrations exceed 1 mg/L at 47% of 251 operating sites in California, 63% of 153 Texas sites and 82% of 41 Maryland sites.

MTBE time series data were available for 29 Southern California sites and 26 sites from Maryland and other Eastern states. These data were evaluated to determine concentration versus time trends for monitoring wells at the downgradient edge of the plume. Time series data suggest 50% to 65% of the sites have stable or decreasing MTBE concentration trends at the leading edge of the plume. MTBE concentrations are more likely to increase than benzene at the downgradient edge of the plume, consistent with the known chemical properties of these compounds. However, the highest MTBE concentrations are typically found near the source.

Time series data were used to compare groundwater remediation rates for MTBE, benzene, and xylene for eight Maryland sites. Remediation systems were combined vapor extraction and groundwater extraction. The database included 84 monitoring wells located within the source area. Pre-remediation time series data indicate that years after the release, MTBE remains in the residual NAPL. The regression of concentration versus time during remediation yielded very similar decay rates for the three compounds (varying between 0.34 and 0.39% per day). Dissolution and volatilization of MTBE does not occur as rapidly as would have been calculated.

However, groundwater remediation was effective, with average concentration reduction of 95% for MTBE, 94% for benzene, and 92% for xylene. These data also suggest air-based remediation systems can be effective years after the release occurred.

References

Mace, R. E., R. S. Fisher, D. M. Welch, and S. P. Parra. 1997. "Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas." The University of Texas at Austin, Bureau of Economic Geology, Geological Circular 97-1, 52 p.

Rice, D. W., R. D. Grose, J. C. Michaelson, B. P. Doohar, D. H. MacQueen, S. J. Cullen, W. E. Kastenberg, L. G. Everett, and M. A. Marino. 1995. "California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses." Lawrence Livermore National Laboratory, Environmental Protection Department, UCRL-AR-122207, Submitted to the California State Water Resources Control Board.

Environmental Behavior and Fate of Methyl *tert*-Butyl Ether (MTBE)

By Paul J. Squillace, James F. Pankow, and John S. Zogorski

ABSTRACT

When gasoline that has been oxygenated with methyl *tert*-butyl ether (MTBE) comes in contact with water, large amounts of MTBE can dissolve; at 25 degrees Celsius the water solubility of MTBE is about 5,000 milligrams per liter for a gasoline that is 10 percent MTBE by weight. In contrast, for a nonoxygenated gasoline, the total hydrocarbon solubility in water is typically about 120 milligrams per liter. MTBE sorbs only weakly to soil and aquifer materials; therefore, sorption will not significantly retard MTBE's transport by ground water. In addition, MTBE generally resists degradation in ground water. The half-life of MTBE in the atmosphere can be as short as 3 days in a regional airshed. MTBE in the air tends to partition into atmospheric water, including precipitation. However, washout of gas-phase MTBE by precipitation would not, by itself, greatly alter the gas-phase concentration of the compound in the air. The partitioning of MTBE to precipitation is nevertheless strong enough to allow for up to 3 micrograms per liter or more inputs of MTBE to surface and ground water.

INTRODUCTION

Fuel oxygenates are voluntarily added to gasoline to enhance the octane of gasoline in many areas of the United States, and fuel oxygenates have been used since 1988 to improve air quality (Begley and Rotman, 1993) in some metropolitan areas. However, since November 1, 1992, the 1990 Clean Air Act Amendments require areas that exceed the national ambient air-quality standard for carbon monoxide (carbon monoxide nonattainment areas) to use oxygenated fuels during the winter when the concentrations of carbon monoxide are highest. Furthermore, since January 1995, the 1990 Clean Air Act Amendments also require nine metropolitan areas that have the most severe ozone pollution to use, year-round, reformulated gasoline that contains fuel oxygenates. Numerous additional metropolitan areas have chosen to participate in the oxygenated fuels and reformulated gasoline programs.

The U.S. Environmental Protection Agency has a drinking water advisory of 20 to 40 $\mu\text{g/L}$; this advisory is based on taste and odor thresholds. However, this advisory concentration provides a large margin of safety for non-cancer effects, and is in the range of margins typically provided for potential carcinogenic effects. (U.S. Environmental Protection Agency, 1997).

MTBE has been detected in ground water (Squillace and others, 1996) and stormwater (Delzer and others, 1996) throughout the United States. Of the 60 volatile organic compounds (VOCs) analyzed in samples of shallow ambient ground water that were collected from eight urban areas during 1993-94 as part of the U.S. Geological Survey's National Water-Quality Assessment program, MTBE was the second most frequently detected compound (after trichloromethane, which also is named chloroform) (Squillace and others, 1996). The ground-water samples were collected from 5 drinking-water wells, 12 springs, and 193 monitoring wells. At a reporting level of 0.2 $\mu\text{g/L}$, MTBE was detected in water from 27 percent of the 210 wells and springs sampled, but no MTBE was detected in water from the drinking-water wells. Measurable concentrations of MTBE also were found in some of 592 stormwater samples collected by the U.S. Geological Survey in 16 cities and metropolitan areas required to obtain National Pollutant Discharge Elimination System permits (Delzer and others, 1996). MTBE was the seventh most frequently detected VOC, occurring in 6.9 percent of the stormwater samples. MTBE had a higher reporting level of 1.0 $\mu\text{g/L}$ for most of the stormwater samples, and it is likely that this resulted in fewer detections when compared to some of the other VOCs that had a reporting level of 0.2 $\mu\text{g/L}$ for all of the samples. Where MTBE was detected, concentrations ranged from 0.2 to 8.7 $\mu\text{g/L}$. Eighty-three percent of all stormwater samples that had detectable concentrations of MTBE were collected between October 1 and March 31. This period of time is approximately when oxygenated gasoline is used in carbon monoxide nonattainment areas.

The purpose of this paper is to discuss the environmental behavior and fate of MTBE. Where appropriate, this report contrasts the properties of MTBE with those of benzene, methylbenzene (also named toluene), ethylbenzene, and xylenes (BTEX compounds). BTEX compounds are present in all gasoline but are the most soluble and toxic compounds associated with nonoxygenated gasoline.

ENVIRONMENTAL BEHAVIOR OF MTBE

Partitioning of MTBE between air, water, and subsurface solids

Volatilization and condensation are the complementary processes that allow the exchange of MTBE across an air-water interface. In this context, volatilization refers to the movement of MTBE from water into the atmosphere, whereas condensation refers to the movement of MTBE from the atmosphere into water. Both processes are driven by concentration gradients between the air and water phases.

When compared to benzene, MTBE tends to partition strongly from the gas phase into the water phase if contaminated air is brought into contact with uncontaminated water. Given sufficient time, equilibrium can be established between concentrations of MTBE in air and water as described by Henry's Law constant, which is temperature dependent. If the same units are selected for the air and water concentrations, then Henry's Law constant is dimensionless. The value of the dimensionless Henry's law constant for MTBE is 0.022 at 25 degrees Celsius ($^{\circ}\text{C}$) (Robbins and others, 1993); a compound with a value of 0.05 or larger would be very volatile from water. Consequently, MTBE tends to stay in the water phase, which explains why MTBE is somewhat difficult to remove from water by aeration. In contrast, the dimensionless Henry's Law constant for benzene is 0.22 at 25 $^{\circ}\text{C}$ (Howard and others, 1990), which indicates that it volatilizes from water and can be removed by aeration. However, the Henry's Law constant alone cannot be used to predict the volatility of MTBE from natural water because in nonequilibrium conditions volatilization also depends on environmental variables such as surface-water turbulence, and to some extent wind velocity.

At this time, there are no known environmental processes that will concentrate MTBE within water or air; however, MTBE will move between air and water until equilibrium is established. Therefore, the concentrations of MTBE in air or water can change with time until equilibrium is established. Furthermore, increased use of MTBE can upset established equilibrium by changing the atmospheric concentrations of MTBE; in general, those metropolitan areas where MTBE is used only as an octane enhancer probably will have lower atmospheric concentrations of MTBE than metropolitan areas where MTBE is added at higher volumes to all gasoline sold to meet the requirements of the 1990 Clean Air Act Amendments.

Water solubility is probably the most important chemical property affecting the partitioning of organic compounds between water and sediment, including subsurface solids. Many organic compounds exhibit water solubilities in the low milligrams-per-liter to micrograms-per-liter range. In general, these low solubilities indicate a strong partitioning to the organic carbon associated with the subsurface solids. However, MTBE is very water soluble compared to the BTEX compounds and other components in gasoline; the solubility of pure liquid MTBE in water is about 50,000 mg/L whereas the next most-soluble component of gasoline is benzene, which has a solubility of 1,780 mg/L (Mackay and others, 1992, 1993).

Once MTBE is in the ground water, it can move at virtually the same velocity as the water, which is one reason why MTBE plumes generally occupy a large portion of the subsurface compared to BTEX compounds. The ratio of the ground-water velocity to the velocity at which a compound is transported is frequently referred to as the retardation factor, R . The actual values of R for a particular compound depend on aquifer properties, such as porosity and organic carbon content. A compound that moves at one-half the velocity of the ground water has an R value of 2. For MTBE, R is fairly close to 1 for typical aquifers whereas the BTEX compounds have R values that can range from 1.1 to about 2.0 (Zogorski and others, 1997); physical and chemical characteristics indicate that compound mobilities generally increase in the following order: xylene, ethylbenzene, toluene, benzene, MTBE (Odermatt, 1994).

Potential sources of MTBE in surface water and ground water

There are point and nonpoint sources of MTBE affecting surface- and ground-water quality. The concentrations of MTBE in water associated with point-source spills can be very large. Gasoline spills to the land surface and releases from above-ground and underground storage tanks are examples of point sources of contamination. As indicated previously, at ambient temperatures the solubility of pure MTBE in water is about 50,000 mg/L (Mackay and others, 1993). However, the solubility of MTBE in water is reduced when other organic compounds are present because MTBE partitions between the organic mixture and water; a gasoline that is 10 percent by weight MTBE, reduces the solubility of MTBE in water to about 5,000 mg/L at room temperature (25 °C) (Barker and others, 1991; Zogorski and others, 1997). In contrast, for a nonoxygenated gasoline, the total hydrocarbon solubility in water is typically about 120 milligrams per liter (Poulsen and others, 1992). The high solubility of MTBE in water combined with its high concentrations in an oxygenated gasoline can result in high concentrations of MTBE in surface water and ground water contaminated by point sources of oxygenated gasoline. Gasoline with MTBE can contaminate large amounts of water; 4 liters of reformulated gasoline mixed with 16,000,000 liters of water will yield 20 µg/L MTBE in the water (Squillace and others, 1997). However, lower concentrations also can result with time if MTBE in the gasoline has been depleted by the dissolution process and the dilution of contaminated water by uncontaminated water.

Potential nonpoint sources of MTBE include precipitation, urban runoff, and motor water craft. Precipitation can be a nonpoint source of MTBE to surface and ground water; moreover, once MTBE is in water it is expected to move between surface and ground water with the natural movement of water. Local gas-phase concentrations of MTBE can be used to predict the concentrations of MTBE in the local precipitation. The amount of MTBE removed from the air by precipitation will not significantly reduce the gas-phase concentration of MTBE in the air; 2.5 cm of precipitation will remove less than 0.5 percent of the MTBE in the air at a temperature of 20 °C (Zogorski and others, 1997). Even though little net loss occurs from atmospheric washout, the loss nevertheless may be important as a nonpoint source of MTBE to water. Although concentrations of MTBE in the air are not frequently measured, concentrations in urban air appear to be on the order of 1 part per billion by volume (ppb-v), or less (Zogorski and others, 1997). The corresponding equilibrium concentration in precipitation at a winter temperature of 5 °C would be 1 µg/L or less. Given higher concentrations such as 3 ppb-v, the equilibrium concentrations in water would be about 3 µg/L (Squillace and others, 1996). Given even higher air concentrations such as 30 ppb-v, the equilibrium concentrations in water would be about 30 µg/L. Elevated concentrations of MTBE in the air immediately surrounding local sources (for example, highways, gasoline stations, parking garages, or refineries) would result in increased concentrations in local precipitation when averaged over months to years.

The concentrations of MTBE and BTEX compounds can lead one to suspect point or nonpoint sources of contamination. Where high concentrations of MTBE and BTEX compounds (greater than 30 µg/L) are detected in ground water, the source of contamination probably is a point source, such as a leaking underground storage tank. The concentrations of MTBE from a point source can be high. For example, MTBE concentrations as large as 200 mg/L have been measured in ground water near a point-source spill of gasoline (Garrett and others, 1986).

When small concentrations (0.2 to 3 µg/L) of MTBE are detected in ground water, the source of contamination may be a point source but more likely is a nonpoint source such as atmospheric washout. MTBE plumes originating from point-source gasoline releases generally occupy a larger volume of the subsurface compared to BTEX compounds, and concentrations of MTBE at the leading edge of a contaminant plume are low but usually increase with time. Therefore, if small concentrations of MTBE were detected in samples at a location contaminated by a point source, then generally one would expect the concentrations of MTBE and detections of BTEX compounds to increase with time at the same location.

Atmospheric washout and water interaction with contaminated road surfaces are possible nonpoint sources of MTBE to surface water, but the concentrations associated with these sources generally are small. As indicated previously, concentrations of MTBE and BTEX were measured in 592 stormwater samples collected by the U.S. Geological Survey in 16 cities and metropolitan areas required to obtain National Pollutant Discharge Elimination System permits (Delzer and others, 1996). The highest concentration of MTBE was less than 10 µg/L and the sum of BTEX concentrations in each stormwater sample was less than 20 µg/L.

FATE OF MTBE IN THE HYDROLOGIC CYCLE

Degradation of an organic compound refers to its transformation by abiotic or biotic reactions. The degradation of organic compounds normally leads to the formation of other organic compounds. The ultimate mineralization (complete breakdown) of an organic compound to carbon dioxide and water can involve many reactions and a long period of time. MTBE can degrade in the atmosphere by various processes including photolysis and reactions with the hydroxyl radical (HO·), ozone (O₃), and nitrate radicals (NO₃·); recent research indicates that MTBE reaction with the hydroxyl radical is the most prevalent (Smith and others, 1991; Wallington and others, 1988). Biological transformations often provide the predominant decay pathways in water and soil, and the complete mineralization of an organic molecule in water and soil almost always is a consequence of microbial activity (Alexander, 1981; Schnoor and others, 1987).

Estimates of the atmospheric half-life (time required for one-half the amount of the compound to degrade) of MTBE can be as short as 3 days in a regional airshed (Smith and others, 1991; Wallington and others, 1988; Zogorski and others, 1997). This estimated half-life assumes a HO· concentration of 10⁶ radicals/cm³ in the regional airshed. However, concentrations of HO· could be lower in air near metropolitan areas, and therefore MTBE could resist degradation until advection carries MTBE outside the metropolitan area. The major degradation product of MTBE in the atmosphere is *tert*-butyl formate. Other degradation products include methyl acetate (acetic acid), acetone, *tert*-butyl alcohol, and formaldehyde (Howard and others, 1996).

BTEX compounds undergo biological transformations; however, many studies have indicated that MTBE does not biodegrade easily under various environmental conditions relating to water and soil. If a research investigation determines that a compound does not degrade, a half-life is not reported and the compound is simply classified as recalcitrant. MTBE is generally reported as recalcitrant and there are no widely accepted estimates of the half-life. Investigators have reported that MTBE is recalcitrant with anaerobic microcosms and under denitrifying conditions, sulfate-reducing conditions, methanogenic-reducing conditions, and anaerobic conditions in landfill-affected aquifer material, soils, and sludges (Fujiwara and others, 1984; Jensen and Arvin, 1990; Yeh and Novak, 1991, 1994; Suffita and Mormile, 1993; Mormile and others, 1994). Nevertheless, degradation of MTBE has been reported on occasion and this indicates that some microcosms are able to degrade MTBE (Thomas and others, 1988; Daniel, 1995). Furthermore, research has demonstrated that bacterial populations and certain pure bacterial strains, when isolated from biotreated sludges and other sources, have the ability to use MTBE as a sole carbon source (Salanitro and others, 1994; Mo and others, 1995). The degradation of MTBE in ground water can lead to the formation of *tert*-butyl alcohol, which has been determined to be a carcinogen in laboratory animals (Cirvello and others, 1995).

Although MTBE can volatilize from water, half-lives in rivers and streams are commonly greater than 1 day, and travel distances range from about 0.8 km for shallow streams to more than 900 km for deep rivers before one-half the MTBE is volatilized (Pankow and others, 1996). Ice on rivers and streams will stop all volatilization of MTBE from the water. Factors that affect the volatilization rate of MTBE in surface water include water velocity, water depth, water temperature, wind speed, and air temperature; in many cases, MTBE volatilizes at rates that are most dependent on the depth and velocity of the flow. No single volatilization rate characterizes the loss process from streams and rivers. In deep and slow moving flows, MTBE volatilizes at rates similar to those for the BTEX compounds. In shallow and fast moving flows, MTBE volatilizes at rates that are significantly slower than those for BTEX compounds (Pankow and others, 1996).

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Fate and Transport of MTBE in Groundwater - Results of a Controlled Field Experiment in Light of Other Experience

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Abstract

A natural gradient test was performed in the shallow, aerobic sand aquifer at Canadian Forces Base (CFB) Borden in 1988. Groundwater containing MTBE and petroleum-derived hydrocarbons was injected below the water table along with chloride (Cl^-) as a conservative tracer. The mass of BTEX compounds in the plume diminished significantly over 476 days due to aerobic biodegradation. MTBE showed perhaps a small decrease in mass. In 1995/96, ground water sampling was undertaken to define the mass of MTBE still present in the aquifer. Only 3% of the original MTBE mass was found. Sorption, volatilization, abiotic degradation, and plant uptake were ruled out as significant attenuation processes. A microcosm experiment provided some suggestion that aerobic biodegradation may have played a major role in the attenuation of MTBE within the Borden aquifer.

Dispersion alone is unlikely to provide sufficient natural attenuation for MTBE. Slow MTBE biodegradation, while difficult to substantiate, may provide sufficient natural attenuation for some MTBE-impacted groundwaters. This uncertainty about MTBE fate in groundwater will mean that remediation using monitored natural attenuation will require substantial ongoing monitoring to demonstrate attainment of remedial goals.

Summary Of The Field Experiment

Intrinsic remediation of gasoline-contaminated ground water generally relies on biodegradation of benzene, toluene, ethylbenzene and the xylene isomers (BTEX) to achieve remedial objectives. Methyl-tertiary-butyl-ether (MTBE), the most commonly used fuel oxygenate, on the other hand, is much more resistant to degradation by microbial populations (Squillace et al., 1997).

A natural gradient tracer test was initiated in the shallow, aerobic sand aquifer at Canadian Forces Base (CFB) Borden in 1988. Groundwater (about 2800 L) containing a mixture of dissolved gasoline-derived hydrocarbons and MTBE was injected below the water table along with chloride (Cl^-) as a conservative tracer. The migration of BTEX, MTBE, and Cl^- was monitored in detail for 16 months. The mass of BTEX in the plume diminished significantly with time, while MTBE showed only a small decrease in mass over the 476 day (16 month) period (Figure 1). MTBE migrated as rapidly as Cl^- (about 9 cm/day), while BTEX were slightly retarded. The experiment is described in detail by Hubbard et al. (1994).

In 1995/96, a comprehensive ground water sampling program was undertaken to define the mass of MTBE still present in the aquifer (Schirmer and Barker, 1998a,b). Since the plume had migrated into an unmonitored section of the Borden aquifer, numerical modeling and geostatistical methods were applied to design a sampling scheme. A drive-point profiling system and a few multilevel wells similar to those used by Hubbard et al. (1994) were used to obtain over 500 groundwater samples. These were analyzed at the Oregon Graduate Institute for MTBE and possible biodegradation products tertiary-butyl alcohol (TBA) and tertiary-butyl formate (TBF) using the methods of Church et al. (1997).

Numerical modeling with consideration of advection and dispersion, but not retardation or degradation, predicted maximum concentrations in excess of 3,000 $\mu\text{g/L}$ could have been found in 1995/96. Maximum concentrations of less than 200 $\mu\text{g/L}$ were found. A mass balance showed that only 3% of the original MTBE mass was found eight years after injection (Figure 1). Sorption, volatilization plant uptake and abiotic degradation are not considered significant attenuation processes for the field conditions. Therefore, we concluded that biodegradation may have played a major role in the attenuation of MTBE within the Borden aquifer (Schirmer and Barker, 1998b).

Laboratory Microcosm Experiment

Lab microcosm experiments using authentic Borden aquifer material and ground water were set up to test the hypothesis that the MTBE disappearance at the Borden field site was indeed caused by biodegradation. Microcosms were incubated aerobically at 10 °C, a temperature typical of the CFB Borden aquifer. Twenty-five aerobic microcosms were set up and repeatedly sampled. Sixteen of the batches were active microcosms (duplicates of eight different tests) whereas nine are sterile controls. Initial results are summarised in Figure 2. Average MTBE concentrations of two sterile controls (SC1, SC2) prepared in triplicate are presented with error bars of one standard deviation. Samples 3A, 3B, 4A and 4B represent the results of duplicate microcosms of aquifer material from two separate aquifer sites.

MTBE concentrations decreased significantly in two, and perhaps in three, active microcosms (3A, 3B and perhaps 4A) in comparison to the sterile controls (SC1, SC2) suggesting MTBE mass loss due to biodegradation. The low MTBE concentrations and high standard deviations on Day 0 for the sterile controls (in comparison to the otherwise relatively consistent concentrations during the other sampling events) probably resulted from non-equilibrated conditions in those microcosms at the start of the experiment.

Apparent Biodegradation of MTBE in the Field Experiment

The lab results presented here seem to confirm the findings of the field study that MTBE biodegraded under Borden aquifer conditions. However, tertiary-butyl alcohol (TBA) or tertiary-butyl formate (TBF), two potential degradation products, were not found in any of the field and lab samples, so direct confirmation of biodegradation was not obtained.

The laboratory results are not considered reliable estimates of actual field biodegradation rates, in part because of the variability in degradation rate within replicates. If we assume that a first-order mass loss rate adequately describes MTBE at the Borden field site, we can calculate a first-order rate based on the initial and final masses using:

$$m = m_0 e^{-\lambda t} \quad (1)$$

and re-arranged as

$$\lambda = -(\ln [m/m_0]) / t \quad (2)$$

where m is the mass at a given time t ; m_0 is the initial mass introduced into the system and λ is the first-order degradation rate. Based on Equation 2 with the values of the Borden field experiment (Schirmer et al., 1998a) of $m_0 = 752$ g and $m = 22$ g at 3000 days, the first-order degradation rate, λ , is 0.0012 day^{-1} .

For the field experiment, Hubbard et al. (1994) calculated first-order degradation rates for the BTEX compounds based on the field mass loss during the first 476 days of the experiment. They report rates between 0.003 day^{-1} for benzene and 0.014 day^{-1} for *m*-xylene, the slowest and fastest degrading BTEX compounds, respectively. For field conditions, those rates are significantly higher than the rate calculated for MTBE. Although those rates represent pseudo degradation rates only and do not describe the true microbial kinetics, they are consistent with the field observations that MTBE was much more persistent than BTEX. The apparent rate of biodegradation based on the field results is much slower than typically observed for BTEX compounds and it is questionable if such biodegradation will be sufficient to protect aquifers and downgradient receptors once MTBE is spilled at a site.

Based on the findings of our MTBE field plume investigation (Schirmer and Barker, 1998a,b) and the preliminary results of our lab microcosm experiments presented here, it is considered plausible that MTBE was subject to biodegradation by the natural microbial populations at Borden. Salanitro et al. (1994) demonstrated that MTBE was biodegradable aerobically. Borden et al. (1997) also claimed MTBE biodegradation occurred in a BTEX plume, based on field and lab observations. The conditions in which MTBE apparently biodegraded were strongly anaerobic, within the BTEX plume and near the source. In our field study, conditions were far less contaminated, with most of the apparent MTBE mass loss occurring after most of the BTEX had biodegraded or had been left behind by the more rapidly advancing MTBE slug.

Possible Significance For Actual MTBE Plumes

To examine the possible significance of MTBE being recalcitrant as opposed to having an apparent mass loss rate of 0.0012 day^{-1} , some simple modeling was done. The modeled aquifer had a groundwater velocity of 9 cm/day horizontal (as does the Borden aquifer). Two types of MTBE plumes were considered:

- 1) a 'slug' of groundwater either 3 m long, 2 m wide, and 1.5 m thick or 10 m long, 10 m wide and 3 m thick, each containing a uniform 269 mg/L MTBE (as injected at Borden), and
- 2) a continuing source of MTBE creating a cross-section source 2 m wide by 1.5 m thick with a constant MTBE concentration of either 269 mg/L (Borden case) or 20 mg/L.

The 'slug' modeling used SLUG3D (Sudicky, 1985) which simulates 3D advective/dispersive transport and can incorporate a first-order decay term, while the continuous source plume modeling used an analytical solution to the advection-dispersion equation having a first-order decay rate (Cleary & Unger, 1994).

The 'slug' modeling determined the time and distance that the centre of mass of the slug would migrate before maximum MTBE concentrations had declined to $35 \mu\text{g/L}$, in the range of typical remediation goals. For the small slug, representative of the actual slug introduced at Borden, longitudinal, transverse (horizontal), and vertical dispersivities of 0.36 m, 0.03 m, and 0.001 m, respectively, were assumed, as found for the Borden aquifer (Sudicky, 1986). With only dispersive attenuation 183 years was required and the centre of mass of the slug had gone about 5000 m (16,400 ft). Assuming additional attenuation via a biodegradation mass loss rate of 0.0012 day^{-1} , the required attenuation was attained in 9.7 years and the centre of mass of the slug had traveled only about 320 m (1050 ft). Note that this is consistent with the actual observations at Borden, where concentrations were $< 200 \mu\text{g/L}$ after about 8 years. Clearly, even a slow biodegradation rate would make a huge difference in the time and distance required to reach typical compliance concentrations ($35 \mu\text{g/L}$ in this case).

At sites where a significant leak of oxygenated fuel had occurred, the initial slug would likely be larger and a more heterogeneous aquifer could be involved. To consider this case, another slug source was considered: 10 m long, 10 m wide and 3 m thick. Again a high MTBE concentration was assumed (269 mg/L), since the 'slug' would likely extract all the MTBE from the fuel. A groundwater velocity of 9 cm/day was retained, but the longitudinal, transverse and vertical dispersivities were increased about tenfold to 3 m, 0.3 m, and 0.03 m, respectively. In this case, dispersive attenuation alone reduced the maximum slug concentration of MTBE to $35 \mu\text{g/L}$ within 140 years and 4600 m (1970 ft) travel distance. Including the slow mass loss rate of 0.0012 day^{-1} , reduced the distance over which $>35 \mu\text{g/L}$ concentrations might persist to about 300 m (980 ft), and this was attained in 9.2 years. While this represents considerable natural attenuation, 9.2 years and 300 m (980 ft) will likely be excessive for many site remediation objectives.

The continuous source case is perhaps a worst case scenario for ongoing or recurring leaks and spills. The modeling attempted to predict when and at what distance from the source an essentially steady $35 \mu\text{g/L}$ contour for MTBE concentration occurred. For the no biodegradation case, with only dispersive attenuation, the $35 \mu\text{g/L}$ contour never reached a steady state, i.e., the plume continued to grow over a simulation time of 300 years. With an apparent mass removal rate of 0.0012 day^{-1} , the $35 \mu\text{g/L}$ MTBE contour became steady, after about 15 years and at a distance of about 480 m (1570 ft) from the source for the source concentration of 269 mg/L. With a lower source concentration of 20 mg/L, the $35 \mu\text{g/L}$ MTBE concentration contour migrated only about 320 m (1050 ft) from the source and steady state was reached after 10 years. While the slow mass loss process clearly restricts the plume size (based on a $35 \mu\text{g/L}$ MTBE concentration contour), MTBE plumes were still 320 to 480 m (1050 - 1570 ft) long; too long to satisfy many remediation goals.

These simple cases illustrate the potential importance of even very small mass removal rates for the natural attenuation of MTBE in ground water. Unfortunately, such rates are very difficult to confirm in laboratory microcosm experiments or from plume monitoring. A clear suggestion that biodegradation could occur was provided in the microcosm experiment described previously. In our experience, slow mass removal rates are difficult to demonstrate from ground water monitoring data, even in controlled field experiments. While MTBE biodegradation is possible (Salanitro et al. 1994), and some biodegradation has been seen in microcosm experiments supporting field studies (this study, Borden et al., 1997), compelling evidence that it should be generally anticipated is lacking. Experience to date has not yet converged even to the point of identifying conditions under which MTBE biodegradation is most likely.

Dispersion alone is unlikely to provide sufficient attenuation for remedial goals of near $35 \mu\text{g/L}$ and natural MTBE biodegradation in groundwater does not yet appear to be well documented nor understood. Given this situation, implementing monitored natural attenuation at sites must rely on detailed field observations of

MTBE plume extent, with continued demonstration that remedial objectives are being met. Clearly, if we are going to move to a more confident use of natural attenuation for MTBE plumes, better understanding and demonstration of MTBE biodegradation in ground water must be developed.

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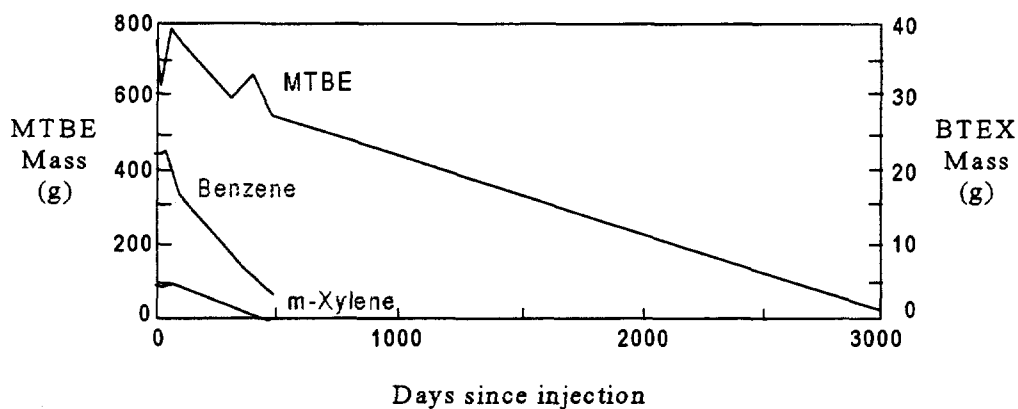


Figure 1: Estimates of Benzene, m-Xylene, and MTBE mass, initially injected and then subsequently found by synoptic sampling over about 8 years. Sorbed and dissolved MTBE mass is included.

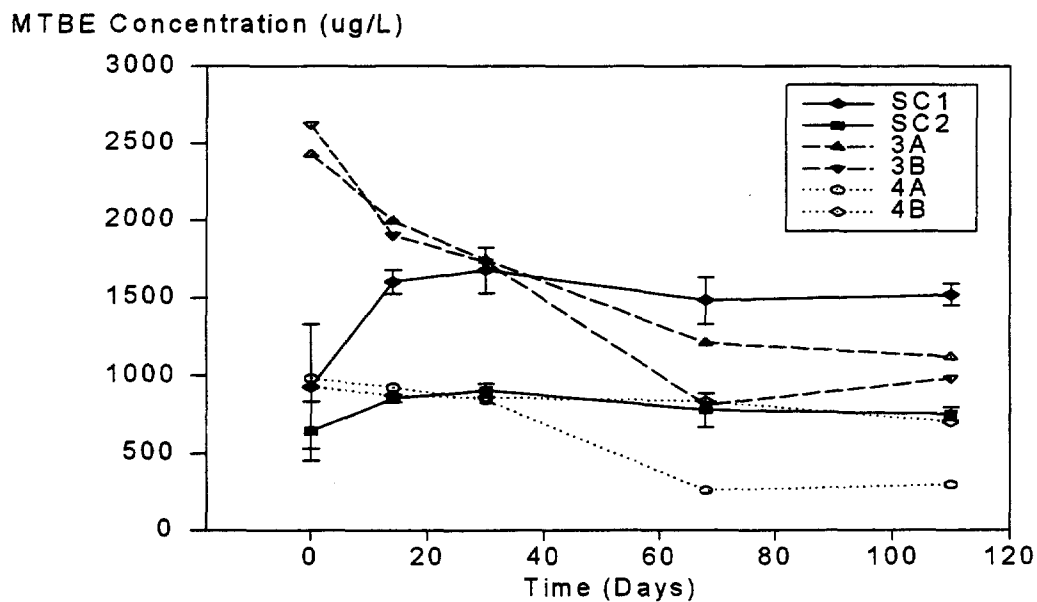


Figure 2. MTBE concentration changes in aerobic microcosm experiments using authentic Borden aquifer material and ground water.

METHYL TERTIARY BUTYL ETHER PLUME EVOLUTION AT CALIFORNIA LUFT SITES

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The use of Methyl tertiary butyl ether (MTBE) as the preferred oxygenate in California Reformulated Gasoline has recently raised concern over potential contamination to shallow ground water. MTBE has been detected at approximately 80% of California leaking underground fuel tank (LUFT) sites previously studied by Lawrence Livermore National Laboratory. Furthermore, at 62% of these sites concentrations exceed the proposed EPA health advisory limit of 70 ppb. Since MTBE is thought to be recalcitrant and highly soluble in water and has only recently been used in large quantities to comply with statewide reformulated gasoline requirements, there is significant interest in the temporal evolution of MTBE plumes in groundwater. In particular, we are interested in determining if observed concentrations and the spatial extent of MTBE plumes are increasing with time and at what rates. To address these issues we are collecting and analyzing time series data from LUFT sites throughout California made available by request from major petroleum distributors. Analysis includes the production of joint probabilistic distributions of observed MTBE concentrations as functions of distance from source location and time as well as distributions of estimated plume length over time. Additionally, temporal trends in well specific concentration levels and site specific plume length estimates are evaluated to predict potential future impacts to groundwater resources. Traditionally, benzene has been considered the contaminant of concern at LUFT sites due to its relatively high solubility and carcinogenic potency. However, the extent of benzene migration is believed to often be limited by biodegradation in groundwater. Parallel analysis of benzene and MTBE plume evolution is presented to compare known and potential impacts resulting from historical releases of the non-conservative contaminant benzene, and recent releases of the potentially recalcitrant contaminant MTBE.

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Methyl *tertiary* Butyl Ether (MtBE) Contamination of the City of Santa Monica Drinking Water Supply - An Update

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Abstract

In the summer of 1996, the City of Santa Monica ceased pumping groundwater from two well fields (Charnock and Arcadia) used for public drinking water supply due to persistent and increasing concentrations of MtBE in all seven municipal water supply wells. This lost production accounted for almost 50% of the City's total drinking water supply. In late 1996, the City, in cooperation with State and Federal agencies, initiated an investigation of MtBE contamination at the two well fields. The results of this investigation were presented in an earlier paper (Brown et al, 1997a; 1997d). The investigation identified more than 30 "possible" sources of MtBE contamination at the Charnock well field, however, the exact sources have not been completely confirmed. An adjacent service station has been identified as the source of MtBE at the Arcadia Well Field. Under the oversight of the Regional Water Quality Control Board (RWQCB), US Environmental Protection Agency (USEPA) and the City of Santa Monica, the responsible parties are now conducting ongoing investigations into the MtBE contamination which resulted in the closure of the well fields.

Shell, Chevron and Exxon have entered into a voluntary agreement with the City to replace the Charnock drinking water supply, investigate contamination at the Charnock well field and implement a source remediation and well field restoration program. Mobil have entered into a similar agreement with respect to the Arcadia drinking water supply. The activities currently underway at Charnock include pipeline testing, a regional hydrogeologic study, individual site investigations, joint USEPA/RWQCB enforcement action, and a treatment technology evaluation. The activities currently underway at Arcadia include a detailed groundwater investigation, decommissioning of the station (including excavation of contaminated soil), treatment of extracted groundwater from the Shallow Aquifer, and a treatment technology evaluation for drinking water. This paper presents some of the preliminary results from these ongoing investigations and remediation programs.

The paper also presents the process by which the impacted well fields are being returned to full production. This includes contaminant source remediation, treatment at the water supply well, and aquifer restoration programs. The regulatory authority directing these programs is discussed, in particular the State Department of Health Services (DHS) requirements for returning an extremely impaired drinking water source to production. It is unknown exactly when the well fields will be returned to production, however, Santa Monica, Mobil and Shell/Chevron/Exxon are committed to the restoration of the Charnock and Arcadia Well Fields, and the ongoing protection of the City's groundwater resources.

Introduction

In the summer of 1996, the City of Santa Monica (the City) ceased pumping groundwater from two well fields (Charnock and Arcadia) used for public drinking water supply due to persistent and increasing concentrations of MtBE in all seven municipal water supply wells. This lost production accounted for almost 50% of the City's total drinking water supply. In late 1996, the City, in cooperation with State and Federal agencies, initiated an investigation of MtBE contamination at the two well fields. The results of this investigation were presented in earlier papers (Brown et al, 1997a; 1997d).

This paper will briefly discuss the impact to the City, the contaminated Charnock and Arcadia well fields, the steps taken to resolve the City's MtBE problem (particularly the regulatory actions), the well field restoration process, and the City's and other water purveyors viewpoint regarding the overall MtBE problem in California.

Other papers have addressed other issues related to the City's MtBE problem, such as details about the City's water supply system (Brown et al, 1997a; 1997d), site specific hydrogeology (Brown et al, 1997a; 1997d), the legal actions taken by the City and the resulting settlement agreements (Patterson et al, 1998), recent legislation in California (Clark et al, 1998), MtBE fate and transport (Brown et al, 1997c), MtBE remediation and drinking water treatment (Brown et al, 1997b; 1997c; 1997e), and the MtBE Research Partnership (Brown et al, 1997b; 1997c; 1997e; Kavanagh et al, 1998). Therefore, this paper will NOT go into any detail regarding these issues.

The Impact on the City Of Santa Monica

The City's drinking water wells are located at three well fields: Charnock (five wells), Arcadia (two wells), and Olympic (four wells). Each field draws water from a different groundwater sub-basin - the Charnock, Arcadia and Olympic Corridor Sub-basins, respectively.

Table 1: City of Santa Monica Water Demand (1990-1997) - The City's Move to Self Reliance

YEAR	GROUNDWATER		MWD		TOTAL (acre/feet)
	(acre/feet)	%	(acre/feet)	%	
1990	4,987	31	11,207	69	16,194
1991	5,592	43	7,404	57	12,966
1992	7,858	58	5,613	42	13,471
1993	9,404	65	5,044	35	14,448
1994	10,037	67	4,953	33	14,990
1995	10,034	70	4,381	30	14,415
MtBE detected at City water supply wells					
1996	5,556	38	9,228	62	14,784
Production Stopped in June 1996					
1997	2,800	18	12,600	82	15,400

In a move toward self-reliance, the City increased it's local groundwater production between 1990 and 1995 (Table 1). This also resulted in a substantial cost saving due to the reduced demand on more expensive MWD water. This trend was reversed in 1996 when contamination by MtBE caused the shut-down of seven municipal drinking water wells at the Charnock and Arcadia Well Fields. The immediate impacts to the City were as follows:

- Loss of 100% of Charnock and Arcadia supply;
- Loss of 71% of local groundwater supply;
- Loss of 49% of total water supply;
- Cost of \$3.5 million to purchase MWD water; and
- Loss of reliable local water supply and a resulting dependence on an external supply.

Regional Geologic Setting

The City's well fields are located in the Santa Monica Structural Basin. The Santa Monica Basin is in the northern portion of the southwestern structural block of the Los Angeles Basin (Yerkes et al, 1965). The Santa Monica Basin is subdivided by faults into five sub-basins (Figure 1):

- The Crestal Sub-basin;
- The Charnock Sub-basin (Charnock Well Field);
- The North Santa Monica or Arcadia Sub-basin (Arcadia Well Field);
- The Olympic Corridor or Central Sub-basin (Santa Monica or Olympic Well Field); and
- The South Santa Monica or Coastal Sub-basin.

A detailed discussion of regional and site geologic setting, hydrogeology and groundwater conditions was presented in Brown et al (1997a; 1997d).

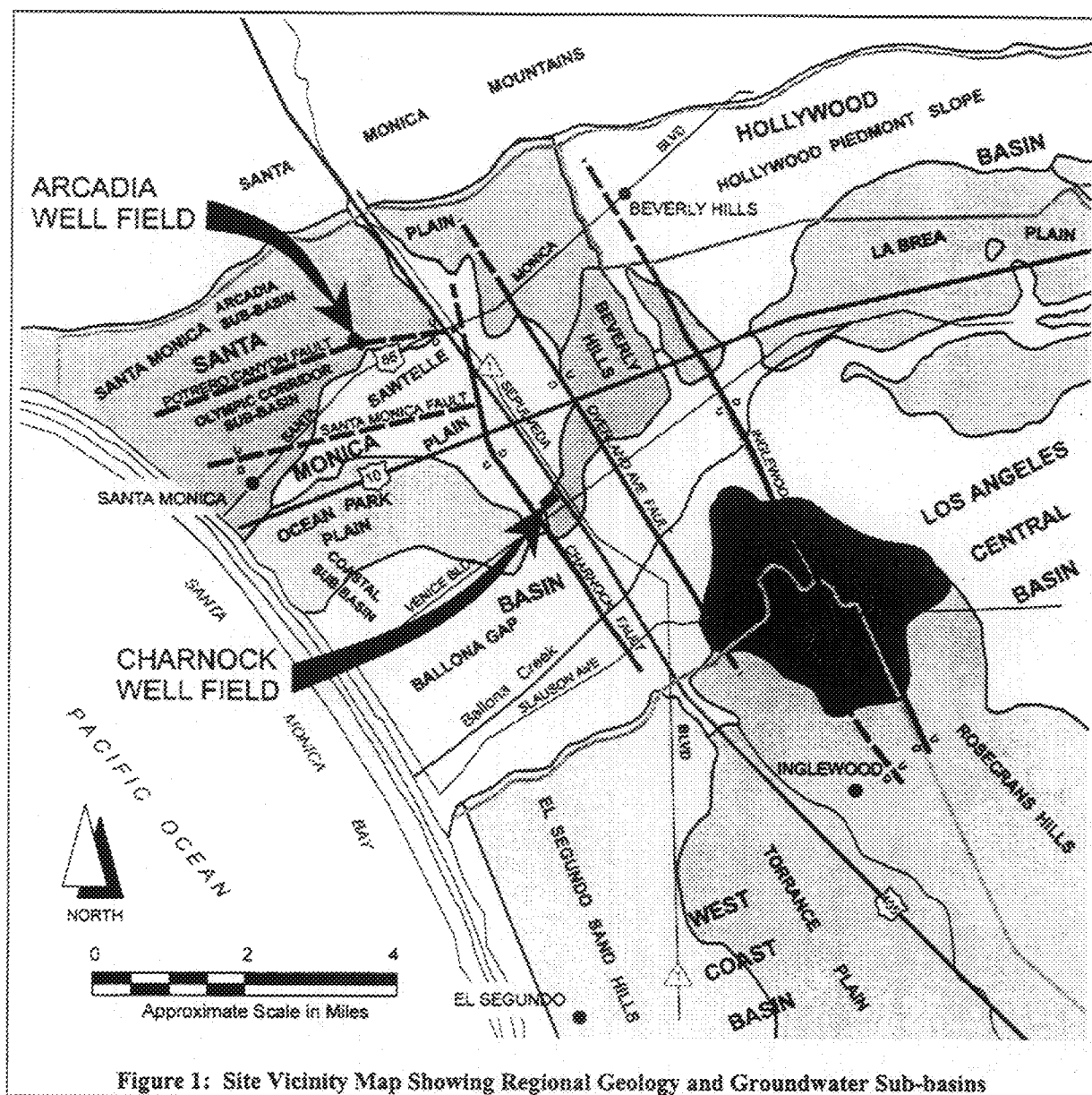


Figure 1: Site Vicinity Map Showing Regional Geology and Groundwater Sub-basins

The Charnock Well Field

The Charnock Well Field is the major source of drinking water for the City. The well field is located at 11375 Westminster Avenue in the City of Los Angeles, approximately 3.5 miles (5.6 km) east of the Santa Monica Bay, 4 miles (6.4 km) south of the Santa Monica Mountains, and approximately 450 feet (137 m) west of the San Diego Freeway (Interstate 405) (Figure 1). Five water supply wells (13, 15, 16, 18, and 19) are located at the site. The well field has a capacity of approximately 8.6 million gallons per day (32,508 m³/day), equivalent to about 6,000 gpm (22,680 L/min). The Southern California Water Company has two wells within the Charnock Sub-basin which provide drinking water the City of Culver City. These wells have a capacity of approximately 2.8 million GPD (10,584 m³/day), equivalent to about 2,000 gpm (7,560 L/min).

MtBE Detection At The Charnock Well Field

MtBE was first detected in groundwater from the Charnock Well Field on August 29, 1995 (Table 2). On March 15, 1996, a maximum MtBE concentration of 610 ug/l was detected at Well #19 (Table 2). On June 13, 1996, all water supply wells in the well field were shutdown due to persistent and increasing levels of MtBE contamination.

Table 2: MtBE Detections at the Charnock Well Field

First Detected:					
Well ID:	13	15	16	18	19
Date:	8/29/95	4/9/96	6/13/96	5/2/96	8/29/95
Conc. (ug/l):	95	53.3	3.1	6.5	8.2
Maximum Detected:					
Well ID:	13	15	16	18	19
Date:	3/26/96	4/15/96	6/13/96	6/10/96	3/25/96
Conc. (ug/l):	490	72	3.1	47.5	610

Potential Sources of MtBE in the Vicinity of the Charnock Well Field

A detailed review of Federal, State and local government databases and agency files was conducted to help identify potential sources of MtBE contamination in the site vicinity and, thus, name potentially responsible parties (PRPs) (Brown et al, 1997a; 1997d). 45 potential source sites were identified: 43 underground storage tank (UST) sites and two refined product pipelines. 33 of these were considered priority sites; that is, they were located within or close to the Charnock Sub-basin, there was evidence or a suspicion of a release, and the sites were operational after 1980. 27 of the priority sites were owned or operated by seven major oil companies (25 UST sites and the two pipelines).

Regulatory Actions

Inter-Agency Task Force

An inter-agency task force, including representatives from Federal, State and local agencies, was established to address the problem of MtBE contamination in the City's drinking water. The USEPA and RWQCB took the lead and developed a memorandum of understanding (MOU) which assigned the agencies the following different responsibilities:

- The USEPA would take the lead, supported by RWQCB, in the regional assessment being conducted by the PRP group. This work would be directed under authority provided in the Safe Drinking Water Act (SDWA), Section 1431, 42 USC 300I, and the Resource Conservation and Recovery Act (RCRA), Section 7003, 42 USC Sec. 6973.
- The RWQCB would take the lead, supported by USEPA, in the individual PRP facility investigation and remediation programs. This work would be directed under authority provided in the Porter Cologne Water Quality Control Act (WQCA), Section 13267.
- Both agencies, along with DHS, would be involved in directing the well field and aquifer restoration program implemented by the PRP groups.

Individual PRP Investigations

The individual PRP investigations must follow the following standardized approach developed by the inter-agency task force, and be performed in accordance with procedures specified in a standardized work plan prepared by the task force (CRWQCB, 1997):

Step 1: Records review

- is the site within the suspected source area?
- was gasoline used/stored at the site after 1980?

- Step 2: Release History

- is there a lack of evidence to confidently determine that no release has occurred at the site?

- Step 3: Soil gas survey

- were hydrocarbons detected during a soil gas survey?

- Step 4: Soil and groundwater investigation

- is MtBE present in soil and/or groundwater beneath the site?

If the answer is YES to the question(s) within a step, the PRP must move to the next step. If the answer is YES to all of these questions, then the PRP will be part of the consent decree and must bear a portion of the costs for the overall well field and aquifer restoration program.

Conclusions - Charnock

The following conclusions can be made for the Charnock Well Field:

- Numerous sources of MtBE exist in close proximity to the well field (Brown et al, 1997a; 1997d);
- Likely migration pathways between these sources and the well field have been identified (Brown, 1997a; 1997d);
- Further regional assessment and numerical modeling is required to confirm the migration pathways (ongoing);
- The City, USEPA, RWQCB, DHS, and the active PRP group (Shell, Chevron and Exxon) are committed to the restoration of the well field and the City's groundwater resources, and are currently implementing a well field and aquifer restoration program;
- Recalcitrant PRPs who have discharged MtBE to soil and/or groundwater must bear a portion of the cost of the well field and aquifer restoration program.

Arcadia Well Field

The Arcadia Well Field is located at 1228 South Bundy Drive in the City of Los Angeles, approximately 3 miles (4.8 km) east of the Santa Monica Bay, 2.25 miles (3.6 km) south of the Santa Monica Mountains, approximately one mile (1.6 km) west of the San Diego Freeway (Interstate 405), and approximately 1,250 feet (381 m) east of the eastern boundary of the City of Santa Monica (Figure 1). Two water supply wells (4 and 5) are located at the site. The well field has a capacity of approximately 0.86 million gallons per day (3,251 m³/day), equivalent to about 600 gpm (2,268 L/min).

MtBE Detection at the Arcadia Well Field

On August 28, 1995, an MtBE concentration of 47 ug/l was first detected in groundwater abstracted from Arcadia #5. A maximum MtBE concentration of 86.5 ug/l was detected at Arcadia #5 on August 27, 1996, and on September 4, 1996 the well was shut down. On October 17, 1996, an MtBE concentration of 19 ug/l was detected in groundwater from Arcadia #4, and the well was shut down on the same day.

Regulatory Actions

At Arcadia, the RWQCB has taken the lead, supported by USEPA, in the investigation and remediation program undertaken by Mobil. Both agencies, along with DHS, are involved in directing the well field and aquifer restoration program implemented by Mobil.

Contaminant Investigation

The most likely source of this contamination is a former Mobil service station located immediately north of the

Arcadia Well Field beyond an alley (Figure 2). In response to a clean-up and abatement order issued by the RWQCB, Mobil has been conducting the following activities at the site:

- Removal of USTs and associated piping and dispensers (complete);
- Demolition of the station building (complete);
- Excavation of contaminated soil at the station to a depth of about 10 feet (3.0 m) (complete);
- Delineation of vadose zone contamination beyond the station property (complete);
- Assessment of hydrogeologic and contaminant conditions to delineate the extent of MtBE contamination in groundwater (the extent of MtBE contamination in groundwater is presented in Figure 2), and help evaluate the migration pathways from the release to the production wells (ongoing);
- Numerical groundwater flow and solute transport modeling to assist in pathway evaluation and remediation design (ongoing);
- Installation and operation of an interim pump and treat system for the shallow aquifer beneath the Mobil station (complete);
- Evaluation of treatment technologies for drinking water contaminated by MtBE through the MtBE Research Partnership (Brow et al; 1997b; 1997c; 1997e; Kavanagh, 1998); and
- Design of remediation systems for the Lower and Production Aquifers (ongoing).

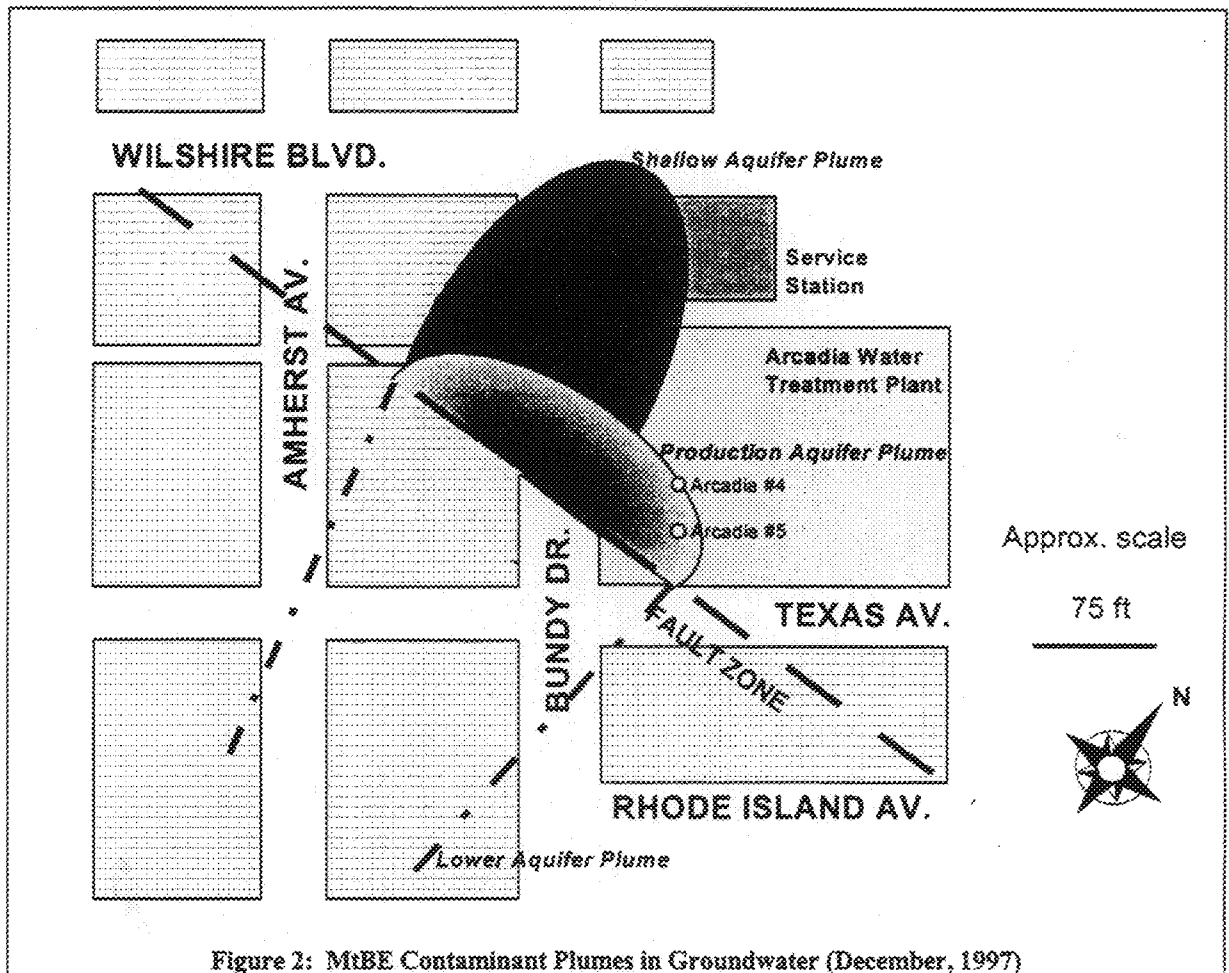


Figure 2: MtBE Contaminant Plumes in Groundwater (December, 1997)

Site Hydrogeology

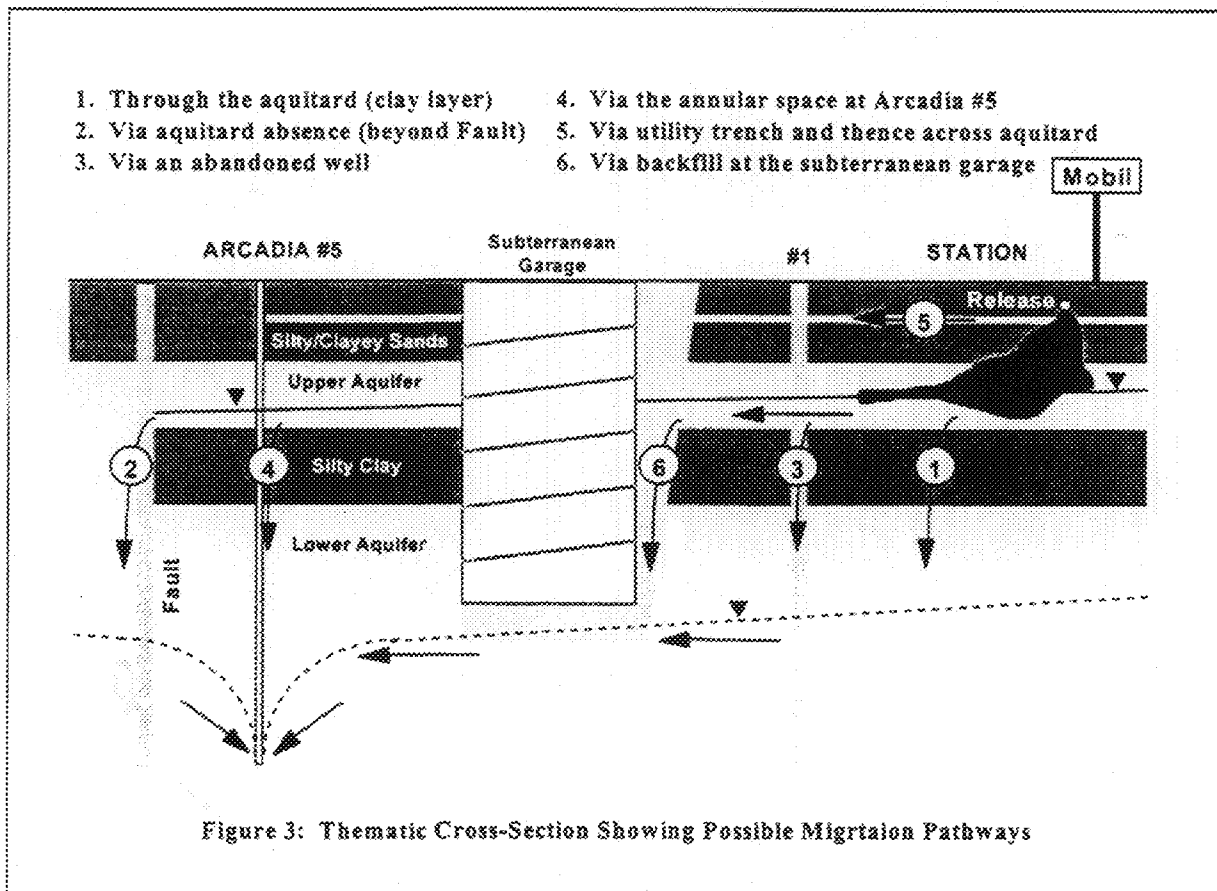
The extreme southern portion of the Arcadia Well Field is located to the south of the Potrero Canyon/Brentwood Fault Zone in the Olympic Corridor Sub-basin. The San Pedro Formation is absent north of the Fault Zone and in the area immediately south of the Fault Zone. The following stratigraphic sequence is apparent north and south of the Fault Zone:

Lithology	North	South
	Elevation (feet)	
Surficial Fine-grained Unit (Holocene Alluvium)	240 - 227	240 - 227
Shallow Aquifer (Holocene Alluvium)	227 - 215	Absent
First Aquitard (Holocene Alluvium)	215 - 180	Absent
Lakewood Formation Aquifer (Upper Pleistocene)	180 - 40 (Production)	227 - 100 (Lower)
Pico Formation First Aquitard (Pliocene)	40 - ?	100 - 50
Pico Formation Lower Aquifer (Pliocene)	?	50 - 25
Pico Formation Second Aquitard (Pliocene)	?	25 - ?

Groundwater movement within the Arcadia and Olympic Corridor Sub-basins is essentially due south at a rather steep gradient. It appears that the Fault Zone may act as a barrier to groundwater flow between the Lakewood Formation Aquifers either side of the Fault Zone, as evidenced by the difference in potentiometric groundwater elevations either side of the Fault Zone (230 feet [70.1 m] above mean sea level [MSL] to the north and 130 feet [39.6 m] above MSL to the south). However, it does not appear to be a barrier to groundwater flow from the Shallow Aquifer to the Lakewood Formation Lower Aquifer south of the Fault Zone, as evidenced by the MtBE contamination present in groundwater to the south of the Fault Zone.

Potential MtBE Migration Pathways

The following potential migration pathways from the release at the former Mobil station to the Arcadia Wells #4 and #5 are currently being evaluated (Figure 3). The exact migration pathway cannot be speculated upon until the hydrogeologic assessment, contaminant delineation and numerical modeling are complete.



Conclusions - Arcadia

The following conclusions can be made for the Arcadia Well Field:

- The source of the MtBE contamination has been determined (Brown et al, 1997a; 1997d);
- Likely migration pathways between these sources and the well field have been identified (Brown, 1997a; 1997d);
- Further hydrogeologic assessment and numerical modeling are being conducted to confirm the migration pathways and assist in remedial design (ongoing); and
- The City, USEPA, RWQCB, DHS, and Mobil are committed to the restoration of the well field and the City's groundwater resources, and are currently implementing a well field and aquifer restoration program.

Steps Taken to Resolve the City's MtBE Problem

The City addressed its MtBE problem by using all available avenues, including the following:

- City implemented investigations (Brown et al, 1997a; 1997d);
- Regulatory involvement (discussed herein);
- Legal actions and settlement agreements (Patterson et al, 1998);
- Legislation (Clark et al, 1998);
- Publicity and public relations (Clark et al, 1998); and
- Research Partnerships (Brown et al, 1997b; 1997c; 1997e; Kavanagh, 1998).

Of these courses of action, only the regulatory involvement will be discussed herein, the other courses of action are addressed in other papers (as indicated above). The objectives of the investigations, regulatory actions, and research partnerships were as follows:

- Identify and screen potential sources of MtBE contamination in the vicinity of the well fields accomplished through the City's investigation (Brown et al, 1997a; 1997d) and individual site assessments conducted by potentially responsible parties (PRPs) at their facilities under the direction of the RWQCB;
- Assess the pathways by which releases at PRP facilities could have contaminated the well fields accomplished through regional hydrogeologic investigations performed by the PRP group at Charnock under the direction of the USEPA, and Mobil at Arcadia under the direction of the RWQCB;
- Evaluate the alternative technologies for removal of MtBE from drinking water accomplished through City sponsored research and the MtBE Research Partnership (Brown et al, 1997b; 1997c; 1997e; Kavanagh, 1998);
- Implement well field restoration programs and source remediation programs mandated by voluntary settlement agreements between the City and Shell/Chevron at Charnock and Mobil at Arcadia, and performed under the direction of DHS, USEPA and RWQCB.

Well Field Restoration Process

In November 1997, the DHS prepared policy guidance memorandum (97-005) for the direct domestic use of extremely impaired drinking water sources. This guidance document outlined the general conditions and a 12 step process that would have to be met to receive a permit to use an extremely impaired drinking water source for domestic supply. The drinking water "source" is considered the production well(s) and the aquifer(s) from which they draw. Memo. 97-005 states that the DHS subscribes *"to the basic principle that only the best quality sources of water ... should be used for drinking."* The memorandum goes on to say that *"these sources should be protected against contamination."* DHS recognizes that *"the use of contaminated water as a drinking water source always poses a greater health risk and ... the use of an extremely impaired source*

should not be approved unless the additional health risks ... are known, minimized, and considered acceptable." In addition, DHS clearly states in the memorandum that *"drinking water quality and public health shall be given greater consideration than costs."*

Extremely Impaired Source (Groundwater)

A groundwater source is considered extremely impaired if it meets one or more of the following criteria:

- Contaminant concentrations exceed ten times the maximum contaminant level (MCL) or action level (AL) established for chronic health effects;
- Contaminant concentrations exceed three times the MCL/AL established for acute health effects;
- The source is threatened due to proximity to known contaminating activities;
- The source is impacted with a mixture of contaminants (e.g. MtBE and PCE); or
- The well is specifically designed to intercept contaminants.

DHS Permit Process

The permit application requirements to use an extremely impaired source for domestic consumption include the following nine tasks:

1. Source Water Assessment
 - *Capture zone determination*
 - *Contaminant source identification*
 - *Resource vulnerability*
2. Raw Water Quality Characterization
3. Source Protection Program
 - *Inter-agency basin management plan*
4. Monitoring and Treatment
 - *Treatment technology evaluation and demonstration (MtBE Research Partnership)*
5. Risk Evaluations
 - *Probability Analysis*
 - *Fatal flaw risk analysis*
 - *Human health risk assessment*
 - *Risk reduction plan*
6. Alternative Source Identification
 - *Risk evaluations for Metropolitan Water District of Southern California (MWD) and Los Angeles Department of Water and Power (DWP) water*
7. California Environmental Quality Act (CEQA) Review
8. Permit Application
9. Public Hearings

The City, as the utility providing water to the consumers, is the permit applicant. Mobil and Shell/Chevron/Exxon are working with the City to collect and analyze the information necessary to obtain the DHS permit in accordance with policy 97-005.

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**SANTA CLARA VALLEY WATER DISTRICT'S
LEAKING UST OVERSIGHT PROGRAM
"MTBE ISSUES IN SANTA CLARA COUNTY GROUND WATER SUPPLIES"**

by
James S. Crowley & Chris Tulloch,
April 21, 1998

ABSTRACT

This paper summarizes the effect of MTBE on groundwater basins in Santa Clara County. Santa Clara Valley Water District (District) is the water resource management agency for Santa Clara County and is located in the southern part of the San Francisco Bay in Northern California. The District meets the wholesale water supply needs for a population of approximately 1.7 million.

The District is unique in that it is a water wholesaler and has a local oversight program contract with the State Water Resources Control Board (SWRCB) to provide regulatory oversight of corrective actions at underground fuel storage tank release sites. As a local oversight program, the District has made significant progress in closing low risk sites and sites that have performed appropriate corrective action to reduce contamination to below levels of regulatory concern. Regulatory closure is granted to sites using a risk based decision making process when the site no longer poses a threat to human health, safety, water resources, or the environment. Over 2,030 cases have been reported to the District and of these some 60% (1230) have been closed. The majority of the cases reported to date have impacted to groundwater.

Over the past three years, MTBE has emerged as a significant contaminant at fuel leak sites within Santa Clara County and has caused increased concern for the protection of drinking water production aquifers. Groundwater provides about 40% of the County's water supply (60% in drought years). The District has taken a progressive and vigilant approach to protecting groundwater resources from MTBE through the use of GIS to manage and analyze both UST site and regional information and in demanding a more intense and detailed level of work be performed at high priority MTBE release sites. The District is also concerned about the significant presence of MTBE at some operating gasoline stations. At the beginning of 1998, Great Oaks Water Company, a local water retailer informed us that MTBE had been detected in one of their municipal supply wells at low concentrations. Additional follow-up at two nearby operating gasoline station sites is revealing how vulnerable municipal drinking water wells really are to MTBE contamination.

Introduction

The District has been actively involved with leaking UST issues since 1981 when releases of chlorinated solvents impacted drinking water wells in South San Jose. During the mid 1980's the District provided technical assistance to the San Francisco Regional Water Control Board relative to investigation and cleanup of solvent cases and the protection of groundwater. In 1987, the District formally undertook a local oversight program, initially as a pilot, to ensure that releases of fuels from USTs were investigated and cleaned up.

Over the past three years MTBE has emerged as a significant groundwater protection issue and has resulted in a change in strategy and priorities for District staff. The occurrence of MTBE within Santa Clara County's groundwater basins is discussed in relation to the following three areas:

- A. Local Oversight Program for Leaking UST's
- B. Issues related to Operating Gasoline UST's
- C. Detection of MTBE in Great Oaks Water Company Well #3

Local Oversight Program for Leaking UST's

The District's UST Program oversees the investigation and cleanup of reported UST petroleum releases. Since the inception of the UST Program, approximately 2,030 fuel leak releases from UST's have been reported in Santa Clara County. Currently, approximately 60% of these releases (1,230) have received formal regulatory closure. Closure is granted by District staff or the Regional Water Quality Control Board when the case no longer appears to pose a threat to water resources, human health, safety, and the environment.

Currently, the District's UST program actively regulates about 830 cases. Of these, approximately 490 cases involve a release of gasoline to groundwater. Approximately 85% of these cases monitor for MTBE (414). Over 300 (70%) of the cases monitoring for MTBE have detected MTBE. The occurrence of MTBE at leaking UST sites is shown on Table 1. Table 2 shows the range of concentrations of MTBE detected at leaking UST sites.

Table 1 - LEAKING UST CASES WITH MTBE

Total Groundwater Cases:	611
• # Gasoline:	485+
• # Monitoring for MTBE:	414
• # With Detection of MTBE:	288
➔ 85%+ cases monitoring for MTBE	
➔ 70% of cases monitoring for MTBE detect it.	

Table 2 - RELATIVE CONCENTRATION OF MTBE AT LEAKING UST SITES

<u>Highest Groundwater MTBE Concentration (ppb)</u>	<u>No. of Sites</u>
>1- 35	42 (15%)
35 - 350	75 (26%)
350 - 3,500	101 (33%)
3,500 - 430,000	70 (24%)

The San Francisco Regional Water Quality Control Board (Regional Board) issued an informal request for MTBE monitoring in a letter to local agencies on May 2, 1995. They formally requested MTBE monitoring at gasoline fuel leak sites on January 12, 1996.

The District has complied with the requests of Regional Board staff and sent information to responsible parties and consultants regarding MTBE monitoring. In December 1996, District staff re-stated the MTBE monitoring requirements and sent letters to all responsible parties, consultants, and local implementing agencies clarifying the Regional Board requirements. On March 2, 1998 the District formally notified all responsible parties and consultants to undertake monitoring of other ether oxygenates that may have been used within the County. These oxygenates include TAME, ETBE, DIPE, and TBA. The Central Valley Regional Board is the only other agency requiring analysis of these other oxygenates.

Prior to July, 1997, District staff had not specifically required significant changes in how MTBE sites were investigated relative to other fuel contaminated sites. Empirical evidence on the behavior of MTBE plumes, related USGS research, and theoretical analysis, suggested that a change in investigative strategy was necessary. District staff undertook development of a new guidelines for MTBE sites. The Federal EPA's March 1997, Expedited Site Assessment document provided much needed information and guidance on how to properly and cost-effectively conduct the types of investigation necessary to appropriately investigate an MTBE plume in groundwater. Using the principles and concepts embodied in that document and relying on the collective experience of staff, the District formally issued guidelines for investigation and cleanup of MTBE sites in the form of the District's MTBE model letter during July 1997. Prioritization criteria for MTBE cases were also established. The model letter and additional guidance has become a model for undertaking MTBE investigations in many parts the United States and is available online at District's UST program webpage at <http://www.scvwd.dst.ca.us/wtrqual/ustmtbe.htm> Since July 1997, staff have been requesting considerably more work at MTBE release sites that pose risks to water supply wells and deeper water production aquifers.

District staff are concerned that there appears to be a certain lack of knowledge within the oil industry and consulting industry relative to how to properly investigate and cleanup MTBE releases based upon the quality and level of investigation performed at MTBE sites. It appears that those industry staff responsible for conducting investigations are not aware of the behavior of MTBE in groundwater nor the issues associated with treatment of water either at the source of the release or at the wellhead. In addition, staff perceive as a failure within the oil industry to commit appropriate resources to investigate MTBE release sites to ensure that water production aquifers are not impacted. Throughout California, most regulatory agencies only require monitoring for MTBE at the present time. There appears to be no consistent statewide effort to appropriately investigate or cleanup MTBE in groundwater and no statewide guidance of any kind. The California legislature has stepped in to provide legislative direction on the urgency and seriousness of the MTBE issue in groundwater. During 1997, AB 592 (Kuehl), AB 1189 (Hayden), AB 1491 (Cuneen), and SB 521 (Mountjoy) all addressed the issue of MTBE impact on water. District staff have also experienced problems in ensuring appropriate MTBE investigations are conducted promptly by industry related to lack of adequately trained consultant personnel and limitations in availability of appropriate drilling equipment locally. A lack of coordination appears to be evident among the oil companies in situations where plumes may be commingled or where it appears to be appropriate for the respective companies to work together in understanding local groundwater flow issues.

Within the District, limitations in staff resources and program budgets have hampered the program's ability to ensure that high priority sites are performing necessary investigations in a prompt manner. However, staff are encouraged that the pace of investigation at sites is picking up as more MTBE specific work is undertaken and industry and consultants learn to perform work in accordance with the new guidelines. A considerable amount of staff time is spent explaining the new requirements to consultants and industry and providing oversight of high priority case investigation and cleanup strategies.

Water retailers have been required to perform monitoring for MTBE in their drinking water wells beginning in February, 1995. The majority of municipal wells appear to have been tested although the monitoring frequency in some of these wells may be as little as every three years. Great Oaks Water Company (Great Oaks) is the only retailer to report detectable MTBE in one of their wells. Great Oaks Well #3, which was sampled on a quarterly basis, had MTBE in November and December of 1997 at levels of 1.5 parts per billion (ppb) and 1.6 ppb respectively. Well #3 was shut down as Great Oaks Water Company has a corporate policy to not deliver any water with detectable contamination to customers. It is our understanding that testing for MTBE has not been undertaken in private wells or smaller drinking water systems within the County. The leading edge of MTBE plumes may have already migrated to other public water supply wells but may not be detectable because of dilution within wells pumping at high flow rates. The District is concerned about the potential for additional water supply well impacts and that migration of MTBE from shallow groundwater zones to production aquifers may have already occurred. Additional work is being proposed to assess whether domestic wells have been affected.

District staff are also participating on the State Boards' Advisory panel on 1998 tank standards commissioned by Governor Wilson (discussed separately later) and on the State Board's GIS and Mapping Advisory Committee. As part of AB 592 (Kuehl) and AB 1189 (Hayden) \$400,000 has been allocated to 2 pilot projects (one in Santa Monica and one in Santa Clara Valley) for implementation of GIS to protect groundwater resources. District staff are working with the State Board and their contractor Lawrence Livermore National Laboratory as well as the Advisory Committee and hope to enhance our current GIS capabilities and build a regulatory decision system that will allow us to prioritize MTBE cases and identify vulnerable wells. Other strategic issues identified by the advisory committee for possible inclusion into the pilot projects include document management systems, electronic reporting of information, and public access to information via the Internet.

The UST Program's strategy for addressing oversight of the investigation and cleanup of MTBE releases is divided into four broad areas; (1) General UST Program, (2) Case Specific Oversight; (3) Data Management and Strategic Planning, and (4) Oversight of Sites near Impacted Well. The major tasks in each of these areas are listed below:

(1) General Program

1. Perform preliminary prioritization of MTBE Cases based upon vulnerability of aquifers and water wells
2. Refine/update guidance for MTBE Investigation (Model Letter)

3. Develop detailed protocol to properly identify the priority of all sites.
4. Perform prioritization of other fuel leak cases relative to MTBE
5. Develop GIS based vulnerability indices for water wells and general areas of the groundwater basin to use in the prioritization of MTBE cases and in targeting currently operating UST's storing gasoline that potentially threaten nearby wells.
6. Develop cleanup criteria to ensure that the groundwater resource is protected.

(2) Case Specific Oversight

1. Ensure compliance with MTBE and ether oxygenate monitoring requirements
2. Ensure that detailed conduit/abandoned well studies are performed at all MTBE sites
3. Issue directives for MTBE investigation and cleanup based upon case priority
4. Provide detailed oversight of highest priority sites
5. Require complete 3-D plume definition at highest priority sites

(3) Data Management and Strategic Planning

1. Enhance GIS to manage data, prioritize cases, and perform vulnerability analysis
2. Develop system for electronic submittal of data and management of documents and data electronically
3. Ensure that staff are trained on latest investigation and cleanup methods
4. Collaborate with ACWA and industry on highlighting research needs
5. Provide public outreach and sponsor educational workshops for consultants and regulated community
6. Update the program's webpage at
<http://www.scvwd.dst.ca.us/wtrqual/ustmtbe.htm>
7. Work with local agencies, universities, and others on cooperative projects
8. Support District legislative efforts

(4) Oversight of Sites near Impacted Wells

1. Provide detailed vigilant oversight of all nearby MTBE source investigations
2. Ensure appropriate level of sampling of all affected and potentially affected water wells
3. Provide oversight of deeper aquifer investigations, deep aquifer testing, contaminant transport modeling, and other local assessment activities
4. Provide oversight on all possible treatment strategies
5. Work with other agencies in ensuring required work is performed
6. Ensure that water wells and the groundwater resource is protected

The outlined strategy may be altered based upon new information relative to MTBE occurrence data, investigation and cleanup technology effectiveness, additional water well impacts, and success of cooperative efforts with others.

Issues related to Operating Gasoline UST's

Over the past year the major focus of this program has changed to monitoring, investigation and cleanup of MTBE which is blended with gasoline. Our MTBE monitoring data shows a disturbingly higher incidence of MTBE detection at UST leak cases with currently operating gasoline tanks than at those cases where the tanks have been previously pulled and are no longer in operation. At sites where operating UST's exist much higher concentrations of MTBE are detected. For example 31% of leak sites with operating UST's have MTBE greater than 3,500 ppb as compared to 6% for sites where there are no longer operating UST's. This information is summarized in Table 3 and shown graphically in Figure 1.

TABLE 3 - MTBE AT OPERATING GASOLINE UST FACILITIES

Total Operating in County:	550+
# with open fuel leak case:	251
# known gasoline release:	223
# gasoline in groundwater:	185
# Monitoring for MTBE:	180
# With Detection of MTBE:	149

→ 83% of operating gasoline facilities with an open fuel leak case that monitor for MTBE detect it. Compare to 59% for non-op facilities.

→ 31% of operating facilities have MTBE >3500ppb. Compare to 6% for non-op facilities.

MTBE AT OPERATING vs NON-OP FACILITIES

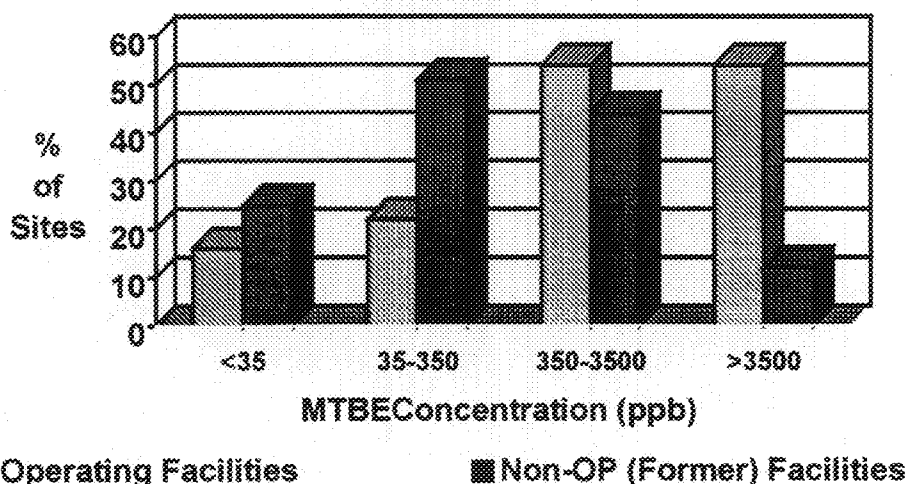


Figure 1 - MTBE at Operating vs Non-Operating UST Facilities

District staff are currently performing an evaluation of recently reported releases to identify whether MTBE releases are occurring at sites with UST's meeting the 1998 requirements. A preliminary report is expected to be completed by July 1998. Some case

specific examples indicate that there may be problems with some UST systems. Staff are working with the local fire departments and the County Health Department in reviewing information relative to new releases from systems and the efficacy of current UST leak prevention and monitoring standards. The District may use the results of this study to develop a strategy to detect releases of MTBE at operating stations and make recommendations to protect groundwater resources.

The District is participating on SWRCB advisory panel commissioned by Governor Wilson to determine if releases are occurring from UST systems that meet the 1998 UST requirements. The panel is to identify appropriate measures that would assure the prevention and detection of oxygenate releases. Preliminary results may be available by the end of 1998.

District staff plan a progressive approach to resolving the issues related to leakage from new upgraded tank systems. First, we will use the results of the two ongoing studies before determining the next appropriate step. Second, we will use information gained in the interim at active stations. The potential strategies which may be developed are:

- A. Cooperative project with the regulated community
- B. District conducts additional studies including sampling at operating tanks. Require monitoring and investigation of MTBE at closed cases which have previously reported a release, but did not sample for MTBE and are still operating gasoline UST's. This may encompass slightly under 100 cases/sites.
- C. Require monitoring for MTBE at operating sites in highly vulnerable areas. This would encompass an estimated 50 to 100 sites.
- D. Require groundwater monitoring for MTBE at all sites which have not reported a release, but are currently operating gasoline UST's. This would encompass over 200 sites.

Detection of MTBE in Great Oaks Water Company Well #3

District staff became aware of the first municipal well impact within the County on January 5, 1998. Dan Stockton, Chief Operating Officer with Great Oaks Water Company called requesting help in understanding why MTBE had showed up in Great Oaks well #3 at 1.6 parts per billion (ppb). The program immediately evaluated the potential sources of MTBE nearby and determined that two gasoline stations located about 500 feet from the well at the intersection of Cottle Rd and Santa Teresa Blvd. Within a week, program staff had met with Chevron and Tosco who operate the gasoline service stations. Both oil companies volunteered to undertake groundwater investigations at their respective sites and committed to additional investigation and cleanup as necessary to put well #3 back into operation. The results of the initial investigations indicated that MTBE was present in the groundwater beneath both sites. District staff and other experts believe any detectable level of contamination is a cause for concern in a municipal well because of the dilution expected at large flow rates. For example, staff believe that the 1.6 ppb MTBE detected in well #3 is indicative of a possible MTBE plume with

concentrations several orders of magnitude higher (100-1,000's ppb) in a deeper zone (aquifer).

Great Oak Water Company had shut down well #3 in mid-December 1997 while they were verifying the initial detection of MTBE at 1.5 ppb from a sample collected at the end of November 1997. Great Oaks has a corporate policy not to deliver any water with detectable contamination to customers. In addition, staff recommended that Great Oaks well #12 be shut down (February 1998) because of proximity to the contamination that affected well #3. Well # 3 draws water from 75 to 270 feet below ground surface. Well # 12 draws water from 50 to 187 feet below ground surface. The shut down of these wells represents a loss in Great Oak's pumping capacity of up to 2,800 gallons per minute (gpm) (4,500 acre-ft/year). These wells pumped approximately 2,200 acre-feet in 1997. Three other Great Oaks wells are in the vicinity of this problem and pumped a combined 4,400 acre-feet in 1997. There is no other immediately accessible source of water for this part of the Great Oaks service area.

TOSCO's initial investigation of groundwater indicated a maximum concentration of MTBE at 420 ppb in a traditionally installed monitoring well. Tosco initially appeared reluctant to perform additional investigation in accordance with our recent guidance due to the low detection in comparison to what had been detected in groundwater at the Chevron site located closer to well #3. A detection of 68 parts per million (ppm) MTBE in soil at the TOSCO site necessitated additional investigation which has shown that up to 140,000 ppb of MTBE exists in groundwater in the vicinity of the UST system. Further investigation has found that MTBE contamination at the site is extensive and extends offsite (extent not yet defined). In addition, wells drilled into the deeper aquifer indicate MTBE contamination of up to 150 parts per billion. Plumes in the shallow and deeper groundwater zones are not defined to date.

The UST's on the TOSCO site are all double walled systems and comply with 1998 standards. Recent testing indicates that these tank systems are not leaking. However, the levels of MTBE detection in the vicinity of the USTs and the lack of appreciable benzene and petroleum contamination is indicative of a newer release that could possibly be related to an undetected escape of MTBE vapor. This vapor transport issue is not well understood by the oil industry and the District has requested that TOSCO take actions to discover the mechanism of release without delay. To date, TOSCO has not been able to provide a reasonable explanation for the presence of the very high concentrations of MTBE at their site.

Based upon current information, it appears that TOSCO is the likely principal contributor to the MTBE contamination in the deeper aquifer that has been detected in Great Oaks well #3. Tosco is being required to perform additional investigation to define the extent of MTBE contamination in both the shallow groundwater zone and the deeper aquifer. They also plan to have a treatment system operational on their site by mid-May 1998. The District program will also be requiring TOSCO to perform additional work relative to investigation and cleanup in the deeper aquifer and well #3. In addition, sampling and aquifer testing of nearby wells, groundwater flow, and MTBE fate and transport modeling

to protect those wells and understand the impact of their release on the groundwater resource in general will be required.

Chevron has conducted significant additional investigation, designed a cleanup system for the MTBE detected at their site, and started operating the cleanup system on April 1, 1998. MTBE has been found at concentrations of up to 11,000 ppb on the Chevron site. Based upon current data, it appears that very little MTBE has moved outside their property boundary in the shallow groundwater zones. They are required to perform additional investigative work to determine if the contamination on their site has moved vertically and contributed to the contamination detected in Great Oaks #3. Chevron has been reluctant to perform the vertical investigation under their source area. Since Chevron appears to date to have possibly contributed to the MTBE contamination in the deeper aquifer, Chevron is required to perform additional work relative to investigation and cleanup in the deeper aquifer and other work as necessary.

The UST's on the Chevron site were replaced with a double walled system (complies with 1998 standards) in November 1994 which has recently passed rigorous testing. Chevron believes that the MTBE contamination observed at their site originated from releases of gasoline from the older tank system at the site since review of chemical analysis performed on soil samples taken during the removal of the former UST's indicated that MTBE was present in subsurface soil at concentrations up to 50 ppm in 1994. The results of recent soil analysis indicate the maximum concentration of MTBE in soil at about 0.13 ppm which appears to indicate that much of the MTBE from the older release has migrated to groundwater.

At present, based upon information available to date, it is difficult to predict how long it will take to cleanup the groundwater in the vicinity of Great Oaks wells #3 and #12. The extent of MTBE in the deeper aquifers has not been defined. Many more months of expensive investigation of the deeper aquifer will be necessary to define the extent of this contamination. The cleanup of MTBE from the shallow groundwater at both the gasoline stations should reduce the mass that can migrate to the deeper aquifer. However, at this stage it is difficult to access when it would be wise to put either #12 or #3 back in service. District staff has undertaken depth discrete sampling of well #3 and confirmed that MTBE contamination is present throughout most of the well screen at concentrations between 0.5 and 1 ppb. Additional hydrogeologic investigation, and definition of the MTBE plume in the deeper aquifer is necessary to allow Great Oaks Water Company to safely continue pumping from the other wells in the area and return to pumping from well #12. The ultimate fate of the impacted well #3 has not been decided.

Conclusions

The increasing occurrence and high concentrations of MTBE in groundwater at fuel leak sites is of great concern to the District. The persistence, solubility, and mobility of MTBE in groundwater, together with the volume in widespread use, has compromised the District's ability to properly protect and manage Santa Clara County groundwater basins. This is a new and very significant water management challenge and potentially large

quantities of groundwater may already have been tainted by MTBE. MTBE and other ether oxygenates pose unique problems in their ability to negatively impact the taste and smell of water at very low concentrations. There are also concerns for health and safety that are still being evaluated by state and federal regulatory agencies. District staff are adopting a very vigilant and aggressive stance with regard to preventing significant contamination through the local oversight program for corrective action at UST sites. Much work remains to be done in understanding MTBE fate and transport at sites and in implementing cost effective investigative and cleanup strategies. District staff are working with the oil industry, other regulatory agencies, and others to address these issues.

The District is also assessing the vulnerability of water supply wells and the potential for MTBE migration from shallow groundwater zones to deeper drinking water production aquifers and into the recharge areas of groundwater basins. Abandoned wells and vertical conduits increase the vulnerability of water supply wells particularly in confined aquifers. The District is using GIS to manage MTBE occurrence data, perform vulnerability analysis, and target areas for detailed investigation.

Overall, District staff see a clear need to respond immediately to prevent further contamination of groundwater resources and protect the public from unnecessary consumption of and exposure to MTBE and other ether oxygenates in their water supply.

On a personal note, the authors believe that regardless of the level at which MTBE causes health effects, it is imperative for the water management community to continue their legacy of groundwater resource protection. We must be relentless in this endeavor. MTBE contamination of water supplies in Santa Clara County has already caused trauma and worry among residents concerned with the safety of their water supply. This human element is not necessarily proportional to the toxicity of this contaminant. Water should be safe, drinkable, and affordable. Young children in a local school were recently heard expressing concern that there were "MTB's", as they put it, in the water they drank at school. Their wish was for this "MTB poison" to be kept out of their water supply. As parents, we tend to agree. Much work remains to accomplish this simple desire.

Mechanism and Efficiency of the Degradation of MTBE in Contaminated Groundwater by the UV/H₂O₂ Process

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Introduction

Since the late 1970's, methyl tertiary-butyl ether (MTBE) has been used as an octane enhancer in gasoline. Because it promotes more complete burning of gasoline, thereby reducing carbon monoxide and ozone levels, it is commonly used as a gasoline additive in localities which do not meet the National Ambient Air Quality Standards.

In the Clean Air Act of 1990, Congress mandated the use of reformulated gasoline (RFG) in areas of the country with the worst ozone or smog problems. RFG must meet certain technical specifications set forth in the Act, including a specific oxygen content. Ethanol and MTBE are the primary oxygenates used to meet the oxygen content requirement.

Studies have indicated that the use of fuels oxygenated with MTBE or ethanol has led to significant air quality and public health benefits. However, MTBE is posing new concerns for drinking water supplies as it has been detected in groundwater and surface water sources in recent years - most notably in Santa Monica (CA), which lost 80% of its local groundwater supply as a result of MTBE contamination in 1996. The city must now spend \$3.3 million annually to buy alternative water supplies. Contamination of groundwater has occurred due to leaks from underground storage tanks (USTs) and pipelines, whereas non-point sources, such as recreational watercraft, are the most likely causes for contamination of surface waters.

MTBE is not currently a regulated drinking water contaminant, as there are currently few data on the effects of drinking MTBE-contaminated water. USEPA has tentatively classified MTBE as a possible human carcinogen based on inhalation studies and is researching the health effects of MTBE exposure. In addition, MTBE has a low taste and odor threshold (anywhere from 15 to 40 ppb). In 1991, The State of California established an interim "action level" of 35 ppb for MTBE in drinking water. The USEPA has recently issued a drinking water advisory to water suppliers for keeping MTBE levels in the range of 20-40 ppb or lower to prevent taste and odor problems and to protect against potential health effects. Finally, the USEPA has included MTBE on a list of contaminants (the Contaminant Candidate List) that may require regulation based on their known or anticipated occurrence in public drinking water systems.

Treatment options for removing MTBE from water supplies include air stripping, activated carbon adsorption, biological treatment, and advanced oxidation (1, 2, 3). Due to its low volatility (high air-to-water ratios) and low affinity to activated carbon, air stripping and activated carbon may not be economical, especially when air stripping systems require off-gas treatment to prevent discharge of VOCs into the atmosphere. MTBE can be biodegraded under certain conditions. However, research is still in the early stages. Moreover, use of biological treatment for potable water treatment is uncertain because of reliability concerns and microbial quality of the treated water.

Advanced oxidation processes (AOPs), such as UV/H₂O₂ and ozone/H₂O₂, are promising and appear to offer the least cost and most practical option. Ozone/H₂O₂ is widely used in Europe for the removal of pesticides from drinking water. However, the use of ozone-based AOPs may be limited in bromide ion-bearing waters, due to the formation of the undesirable bromate ion, a suspected carcinogen.

The UV/H₂O₂ process involves the photolysis of added H₂O₂ to generate hydroxyl radicals (\cdot OH), which then attack and oxidize (with the aid of dissolved O₂) organic pollutants converting them eventually to CO₂ and H₂O. This process has been used routinely for groundwater remediation in over 200 sites worldwide. Its main advantage over ozone-based processes is that it does not form bromate ion (4, 5).

This paper discusses the degradation of MTBE in tap water by the UV/H₂O₂ process from the standpoint of its efficiency. Intermediate oxidation by-products have been identified and quantified, and their relevance to the water industry is discussed.

Experimental

Experiments were performed on Toronto tap water in a standard Rayox 1 kW batch unit, spiked with 0.1, 1.0, 10 and 80 ppm of MTBE. The test with 10 ppm of MTBE was repeated in presence of 0.6, 5 and 13.5 ppm of benzene, toluene and xylenes (BTX). Hydrogen peroxide was added in a dose equal to 30% absorption of the UV light or three times the concentration of MTBE, whichever was higher. This amounted to 25 - 30 ppm peroxide for the 0.1 to 10 ppm MTBE cases and 240 ppm for the 80 ppm MTBE case. Hydrogen peroxide was added and the lamp was ignited. Samples were taken at regular intervals, corresponding to increasing UV doses and analyzed for MTBE and the expected by-products. The analyses were carried out employing a variety of analytical tools and methods, such as GC/FID, purge and trap GC/FID, HPLC and spectrophotometry.

Results and Discussion

As an example of the data obtained, the analytical results for the 80 ppm MTBE are shown in Figure 1, in which *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), acetone, formaldehyde and formic acid are the primary intermediates. We have also detected and quantified methyl acetate, pyruvic aldehyde, glyoxal, acetic acid, pyruvic acid and oxalic acid. A full description of all the intermediates and a total organic carbon balance will be presented in a later paper. Formaldehyde might be of some concern; however, since MTBE is rarely found at concentrations greater than 1 ppm in drinking water supplies, this intermediate would be present at maximum levels much less than 100 ppb and would be destroyed rapidly by the UV/H₂O₂ process. The other detected intermediates do not present any concern as regards toxicity, especially at the low levels encountered.

In all cases, the decays of MTBE and the BTX components were found to follow first-order kinetics. Thus, it is appropriate to analyze the data in terms of the figure-of-merit *Electrical Energy per Order* (EE/O) (6) defined as the number of kilowatt hours of electrical energy necessary to reduce the concentration by one order of magnitude in 1000 US gallons of water. The EE/O may be obtained from the negative inverse of the slope of a plot of $\log(\text{conc.})$ vs. *UV dose* (kWh/kgal) (see Fig. 2). Notice that the EE/O decreases (greater electrical energy efficiency) as the concentration of MTBE decreases. The reason for this is that at higher concentrations the intermediates compete more effectively with MTBE for hydroxyl radicals and thus decrease the overall electrical energy efficiency.

MTBE is often found in ground water with benzene, toluene and xylenes (BTX) as co-contaminants. Thus, we have examined the effect of various concentrations of BTX on the efficiency of treating MTBE. The results are shown in Fig. 3. The EE/O values increase with the concentration of BTX which arises from a competition for hydroxyl radicals between MTBE and the BTX components. However, the amount of the BTX components is less than half that of the MTBE, one sees from Fig. 3 that the treatment efficiency will not be affected significantly by such BTX amounts.

Mechanism

The generation of *tert*-butyl formate (TBF) as a major and early intermediate (see Fig. 1) indicates that the hydroxyl radical attack occurs primarily at the methoxy methyl group and only to a minor extent at the *tert*-butyl methyl groups. Runs starting with TBF indicate that TBA and acetone are formed primarily from the degradation of TBF. Further details on the mechanism will be presented in a later paper.

Conclusions

1. MTBE can be treated effectively by the UV/H₂O₂ process with EE/O values between 2 and 12 kWh/order/kgal, depending on the initial concentrations of MTBE and BTX components.
2. Most of the important intermediates in the UV/H₂O₂ degradation of MTBE have been identified and quantified. None presents any toxicity concerns at the levels involved.
3. The presence of BTX components in the water does adversely affect the treatment efficiency for the degradation of MTBE but only at levels greater than 1 ppm.

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Figure 1. Concentration time profiles in the UV/H₂O₂ treatment of MTBE in Toronto tap water

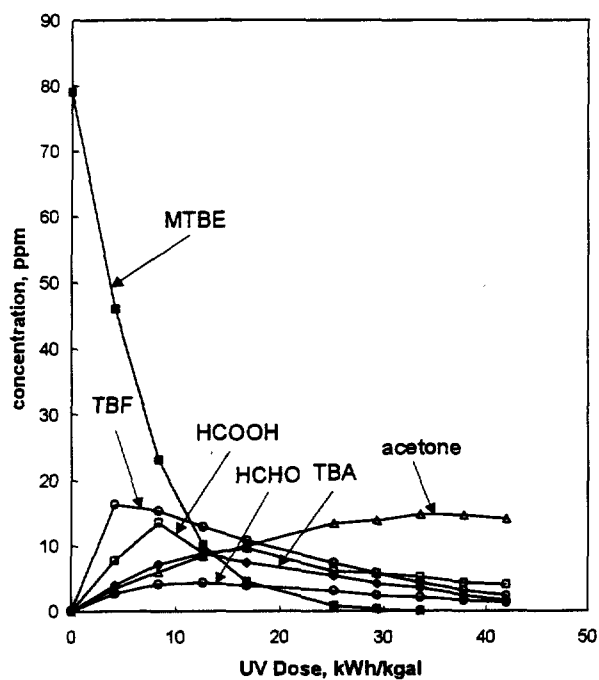


Figure 2. MTBE Decay vs. UV Dose for various initial concentrations of MTBE in the UV/H₂O₂ treatment of MTBE in Toronto tap water

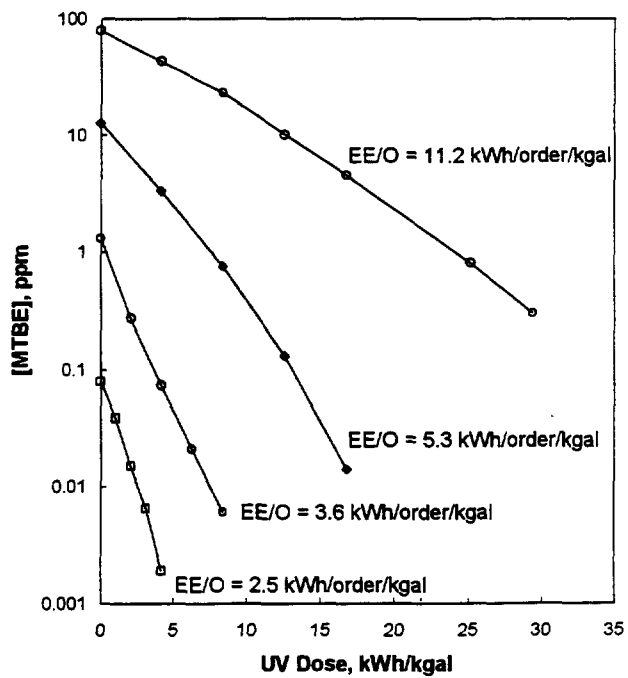
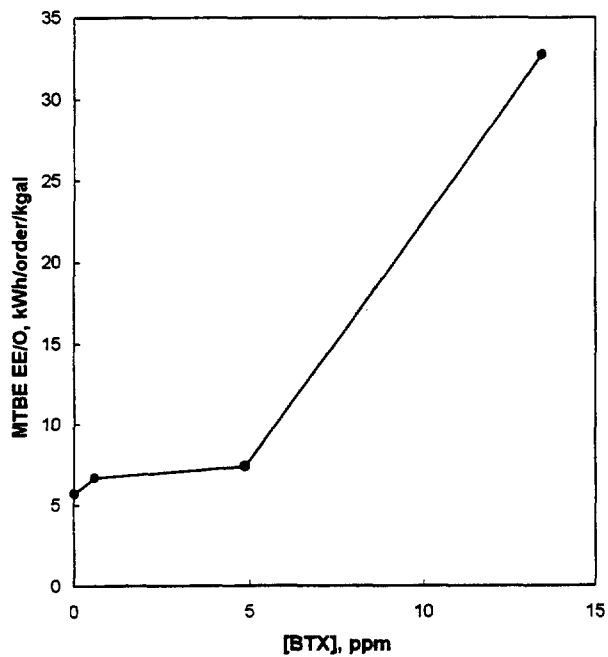


Figure 3. Effect of BTX on the EE/O values for MTBE in the UV/H₂O₂ treatment of 10 ppm MTBE in Toronto tap water



**PERSPECTIVES ON MTBE BIODEGRADATION
AND THE POTENTIAL FOR IN SITU
AQUIFER BIOREMEDIATION¹**

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Abstract

Current knowledge of the microbial breakdown of the gasoline fuel oxygenate, MTBE, by soil and activated sludge culture enrichments indicate that: (1) microbial consortia can be isolated which metabolize MTBE via a pathway in which TBA is only a transient intermediate, (2) degrading cultures grow poorly and slowly on ethers, but metabolite accumulation is usually not observed, (3) biotreatment systems seeded with ether-degraders may be used to destroy MTBE in hydrocarbon-containing wastes (e.g. BTEX) and ground waters, but require longer hydraulic and biomass solids detention periods than conventional units, (4) the presence of indigenous MTBE-degraders in soil and groundwater is low and the enrichment of such plumes for natural attenuation would be limited given the low growth rate of these organisms, and (5) laboratory experiments on the inoculation of groundwater and aquifer sediments with ether-degrading cultures to enhance aerobic MTBE biodegradation suggest that aquifer seeding may be an approach for controlling the leading front of plumes. The stability, persistence and maintenance of ether-degrading activity in the biobarrier, however, remains to be evaluated in pilot-scale field tests.

Perspectives on MTBE Biodegradation and the Potential for In-Situ Aquifer Bioremediation

Introduction

Several metropolitan areas in the U.S. exceed the National Ambient Air Quality Standard for carbon monoxide (CO).⁽²⁸⁾ Under the 1990 Clean Air Act Amendment, however, motor fuels sold in these cities are required to contain oxygenates such as MTBE (methyl tertiary butyl ether) and ethanol (up to 1.8-2.7% by wt. of oxygen) for reducing vehicular emissions of atmospheric CO and ozone-forming compounds. Reformulated gasolines which were introduced in 1992 with the oxygenated fuels program also contributed significantly to improving overall air quality with attendant reductions in VOCs, olefins and sulfur emissions from automobiles.⁽³⁷⁾ Depending upon the study, CO emissions have decreased by 21%⁽²¹⁾, 16%⁽⁸⁾ or 5-10%⁽¹⁴⁾ with the introduction of oxygenate-blended reformulated gasolines.

MTBE is the predominant oxygenate in fuel blends in the U.S., however, it has also been used as an octane-enhancer in varying amounts (1-15% v/v) over the last 15 years.⁽²⁵⁾ In 1986 Garrett et al.⁽¹⁵⁾ reported the presence of MTBE (0.2-236 mg/L) in several monitoring wells from a single underground storage tank release site in Maine. The fuel contained 3% MTBE and the oxygenate had migrated 750 ft downgradient from the spill. Other more recent (1993-1994) surveys of shallow urban ground water in eight cities have indicated that 29% of the wells sampled (210 total) had MTBE only or MTBE and BTEX compounds above the detection limit of 0.2 ppb.⁽⁴²⁾ A health advisory on MTBE issued in December 1997 by the EPA has indicated a safe drinking water level of ≤ 20 -40 $\mu\text{g/L}$ based on the ether's odor and taste threshold.⁽⁴⁷⁾

MTBE plumes have been shown to move with the ambient bulk ground water velocity at fuel release sites. The ether's higher water solubility (43 g/L), low soil sorption coefficient ($K_{oc} = 1.05$) and lower Henry's law constant ($H = 5.8 \times 10^{-4}$ atm \cdot m³/g-mole) and significantly lower biodegradability rate, relative to BTEX components of fuels, can result in the formation of long plumes (up to several thousand feet from source) in sandy and fractured aquifers.^(38,44)

There are relatively few reports on the practical application of ether-degrading cultures or enrichments in the biotreatment of wastewater or ground water containing $\mu\text{g/L}$ or mg/L levels of MTBE and volumetric flow rates of a few to many gallons per min (gpm). The inherent properties of MTBE-degrading cultures (i.e. slow growth and low yield) make it difficult to treat large volumes of MTBE-containing water at different concentrations. One potential application of MTBE-degrading microbes, in-situ, however, is to implant cultures in aquifers as a biobarrier for enhancing the biodegradation of low MTBE concentrations in ground water.

In this paper, we (1) summarize existing literature data on the biodegradability of MTBE and characteristics of ether-degrading systems, and (2) show how an active MTBE-degrading consortium (BC-1) may be used in an aquifer seeding scenario for MTBE plume control.

Microbial Cultures Degrading MTBE

Current evidence for the microbial metabolism of MTBE is summarized in Figure 1. It is presumed that the initial oxidation of MTBE by an oxygenase forms the short-lived intermediate, t-butyl formate (TBF), which undergoes aqueous hydrolysis and/or very rapid microbial breakdown by the consortium BC-1.⁽³⁴⁾ TBF has also been shown to be an intermediate in the degradation of MTBE by the fungus, *Graphium*,⁽¹⁶⁾ and the free radical-initiated oxidation of MTBE in the atmosphere.⁽²⁰⁾ The aerobic oxidation of MTBE to t-butyl alcohol (TBA) has been shown by petrochemical refinery biosludge enrichments^(11,32), a propane-

oxidizing enrichment⁽²³⁾ and the *Graphium* fungal culture grown on butane.⁽¹⁶⁾ More recently, alkyl ethers such as dimethyl and diethyl ethers have been shown to be oxidized to a mixture of their corresponding alcohols and aldehydes by methane-oxidizing⁽¹⁰⁾ and ammonia-oxidizing⁽¹⁹⁾ bacteria. Such a monooxygenase-type activity is presumed to occur in the initial oxidative cleavage of MTBE to form formaldehyde and TBA.⁽⁴³⁾ An anaerobic river sediment enrichment can transform MTBE to TBA only⁽²⁶⁾, however, MTBE (72 mg/L) had no effect on methanogenesis from glucose.⁽²⁷⁾ Recently, Steffan et al.⁽⁴³⁾ demonstrated that propane-oxidizing microbes isolated from soil can oxidize MTBE to TBA and then further metabolize TBA to 2-methyl-3 hydroxypropanol (MHP) and then to 2-hydroxyisobutyrate (HIB). It was suggested that the latter intermediates may be the rate-limiting steps in the metabolism of MHP and HIB to isopropanol since propane-oxidizers grow poorly on these compounds.⁽⁴³⁾ However, our experience indicates that ether-degrading cultures also grow poorly on TBA. The BC-1 consortium is able to rapidly degrade all the downstream intermediates shown in Figure 1 from TBA to acetate.⁽³²⁾ Also, such intermediates are not usually detected in laboratory reactors and soil microcosms which are actively degrading MTBE.

The potential and limits of utilizing MTBE-degrading cultures in bioreactors for ground water and wastewater treating or in-situ remediation can be assessed through an understanding of the characteristics of ether-metabolizing cultures. Table 1 is a summary of physiological and biochemical features of the BC-1 consortium. This bacterial culture contains about 5-6 species of gram-positive and gram-negative microbes.⁽³²⁾ Preliminary screening of selected metabolic genes from BC-1 using DNA probes indicates that the *nah/xyl E* gene (catechol 2,3-dioxygenase at ca. 0.01% of the total cells in BC-1) is present, but it is not known whether this gene is involved in MTBE oxidation (unpublished observations). BTEX degradation activity is also low in this mixed culture. More recently, however, Hur et al.⁽¹⁸⁾ have shown that a toluene-2-monooxygenase in a strain of *Burkholderia cepacia* can oxidize ethyl ether to acetaldehyde and ethanol which supports previously mentioned studies^(10, 19, 23, 43) that a monooxygenase is involved in the primary enzymatic attack of MTBE. Other DNA hybridization probe experiments indicates that the alk B (alkane hydroxylase, C₆-C₁₂) and AMO (ammonia monooxygenase) genes are not readily detected in BC-1 (unpublished data).

The MTBE degrading activity could be consistently maintained⁽³²⁾ in a continuous cell recycle chemostat⁽³³⁾ or porous pot-type reactor⁽⁷⁾ treating MTBE as sole carbon source (100-200 mg/L) in which biosolids (1-5g/L) are retained with minimal loss to the effluent. After a significant period of adaptation (several weeks) ether biodegradation can be observed with effluent removals ≥ 99%. Because of the low growth yield of bacteria on MTBE such bioreactors are necessary to enrich for and retain ether-degrading activity.

In other studies we are attempting to understand why MTBE is an apparent poor growth substrate for activated sludge and soil microbes. Figure 2 is a graph of the heats of combustion versus bacterial cell yields for a selected number of substrates. Data is taken from the studies of Linton and Stephenson⁽²⁴⁾, Bekins et al.⁽⁶⁾, Arvin et al.⁽³⁾ and our own growth experiments with BC-1 on MTBE and other organic compounds. High energy-yielding substrates such as propane and glucose (>9 Kcal/g-C) produce higher cell yields (>1 g cell dry wt./g-carbon) while highly oxidized, low energy-containing compounds (e.g. formate and oxalate) support low cell growth (<0.5g/g-C). However, MTBE (as most alkylethers e.g. TAME, ETBE and DIPE) contain about 12 Kcal energy/g-C, but cell yields are low (0.1-0.3g/g-C) with enrichment cultures utilizing the ether as sole source of carbon.^(11, 32, 43) Such apparent yields are similar to those reported for autotrophs (e.g. nitrifiers) and anaerobically fermenting microbes using alternate electron-acceptors (e.g. SO₄²⁻ and CO₂-reducers).⁽⁴⁾ The proposed stoichiometry for MTBE degradation based on cell yields of 0.2 and a cell composition of C₃H₇NO₂ can be represented by the equation, C₃H₁₂O + 6.5O₂ + 0.2NH₃ → 0.2C₃H₇NO₂ + 4CO₂ + 5.6H₂O. The oxygen demand requirements for growth of ether-degrading cultures on MTBE is, therefore, ca. 2-2.5 mgO₂/mg MTBE. We have also observed that MTBE inhibits its own degradation in BC-1 at concentrations above 5 mg/L. Kinetic experiments show that removal rates (mg/g cells/h) decline with increasing MTBE levels with a significant concomitant rise

in the K_m saturation constant for the ether. We have previously reported on MTBE inhibition in BC-1 in the reduction of ^{14}C -MTBE mineralization to $^{14}\text{CO}_2$ at concentrations of 20 mg/L.⁽³¹⁾

It is not entirely clear why BC-1 or other adapted cultures can apparently metabolize MTBE to CO_2 yet obtain little energy for cell synthesis. The phenomenon of uncoupled growth with substrate utilization ("energy-spilling" metabolism), resulting in "apparent" high maintenance energy requirements has been documented for pure cultures of bacteria growing under conditions in which yields are suboptimal and much less than predicted. Futile cycles of enzyme regulation, K^+/NH_4^+ balance and uptake and those regulating proton circulation for ATP synthesis have been implicated in chemiosmotic imbalances resulting in an inability of cells to generate utilizable energy (e.g. ATP and NADH) for good cell growth on substrates with apparent high energy contents.⁽³¹⁾ Interference of respiratory Na^+ pumps involved in ATP synthesis, symport and antiport substrate uptake systems, electron transport and decarboxylase activity have also been known to uncouple growth in microbial systems.⁽¹³⁾ Ethers, hydrocarbons (aromatic and alkanes) and solvents, however, have been known to dislocate membrane lipoproteins⁽³⁸⁾ reduce Na^+ conductance and increase passive ion diffusion in membranes.⁽³⁹⁾ We have very preliminary evidence that MTBE-cultured cells of BC-1 may be less able to uptake Na^+ ions compared with the consortium grown to high yields on sucrose.

BC-1 degrades other branched alkyl ethers (ETBE, TAME, DIPE) as well as ethyl ether (DEE) and methyl butyl ether (MBE).⁽³⁴⁾ A refinery biotreater enrichment⁽¹²⁾ and propane-oxidizing cultures⁽⁴⁴⁾ have also been shown to degrade related oxygenate ethers (ETBE, TAME). Bacterial strains comprising the BC-1 consortium also grow on isopropanol, acetone, pyruvate and acetate, but grow poorly on TBA (Figure 2).

Studies by Sun et al.⁽⁴⁵⁾ and Tang and Sun⁽⁴⁶⁾ on biotreating mixed wastes or groundwater containing MTBE in BC-1 seeded activated sludge suspended solids reactors indicate that the MTBE-degrading activity is sensitive to low temperatures ($<20^\circ\text{C}$), low pH ($<\text{pH}6$), hypoxic conditions (dissolved oxygen <1 mg/L) and substrate (BOD or MTBE) loadings ≥ 0.1 (F/M). Maximum MTBE removal rates (≤ 100 $\mu\text{g/L}$ effluent MTBE) could be achieved only when hydraulic and cell detention times were ≥ 0.25 -1 and ≥ 20 -25 days, respectively and a maximum loading of 10 mg/L reactor volume/day.⁽⁴⁵⁾ Tang and Sun also showed that a field pilot-scale granular activated carbon fluidized bed (30 gal) reactor seeded with BC-1 could treat MTBE (1,000 $\mu\text{g/L}$) in groundwater to 20-200 $\mu\text{g/L}$ with volumetric flows of ≤ 3.5 gpm and a maximum loading of 10-40 mg/L reaction volume/day.⁽⁴⁶⁾ These data indicate that it may be difficult to consistently maintain MTBE mass removals to very low $\mu\text{g/L}$ levels in biotreatment systems with high flows (e.g. gpm) and short biosolids residence time (e.g. <20 days).

Experiments on the effect of MTBE on indigenous BTEX biodegradation in aquifer soil and ground water microcosms prepared with samples from several sites have shown that aromatic hydrocarbons (1-5 mg/L) degraded at varying rates (0.02-0.4/d) but were not significantly affected by ether levels of 5-90 mg/L.⁽³⁵⁾ These results presented in Table 2 also indicate that (a) intrinsic biodegradation may exist in some ground waters after a lag period under aerobic, but not anaerobic conditions, and (b) high concentrations of MTBE (>30 mg/L) may increase the lag time slightly (7-14 days) before BTEX degradation commences. In other studies, Horan and Brown⁽¹⁷⁾ showed that high MTBE concentrations of 740 mg/L can inhibit (50%) the mineralization of ^{14}C -hexadecane to $^{14}\text{CO}_2$. Substrate competition experiments performed with the BC-1 consortium in which benzene or BTX compounds (1-5 mg/L) were preincubated prior to addition of MTBE (1-5 mg/L) indicate rates of ether degradation were not appreciably affected by the presence of aromatic compounds. These data confirm previous observations^(13, 40) that MTBE is not metabolized by BTEX-degrading microbes and that the presence of BTEX has no effect on ether degradation. In an aquifer or biotreating system, MTBE would compete for O_2 availability when BTEX and MTBE degraders are present in sufficient numbers to affect rapid hydrocarbon and ether degradation. Field-derived intrinsic attenuation rates for MTBE have been obtained by Schirmer et al.⁽³⁸⁾ and Borden et al.⁽⁹⁾ in sandy and clayey-sand aquifers, respectively. Rates of 0.0012/d and 0.001/d were obtained from

long-term monitoring of plumes (several years) and based on horizontal and vertical distribution profiles and 3D modeling of groundwater MTBE levels.

In a survey of biosludges from petrochemical plants and subsoil and ground water samples from retail and refinery locations, we have used simple serum bottle assay systems containing low levels (1-5 mg/L) and adequate O₂ concentrations (air or pure O₂) within the headspace (Figure 3). "Die-away" serum bottle assays can be used to assess maximum ether removal rates and kinetics. Most probable number dilution techniques are also used to determine number of ether-degraders per g or per L aquifer soil or groundwater, respectively. Specific microbial removal efficiencies of MTBE from samples vary in the range of 0.01-1.2 mg/g cells/d for wastewater treatment plant biosludges to 0.05-1.6 mg/L/d for ground water. Refinery sludges contain 1000 X fewer degraders/g biomass and at least 100 - 1,000 X lower MTBE removal rates than BC-1 (Table 3). At these low biodegradation rates, most of the MTBE mass would likely volatilize from aeration basins. MTBE-degrader populations are also usually quite low or not detected (0-100/L) in groundwater or aquifer soils and rates of removal by bioattenuation would be slower than the bulk ground water velocities because of the low growth rates of indigenous or selected ether degraders.

Laboratory Soil Microcosm Observations

We have observed an apparent intrinsic (natural) biodegradation of MTBE in a few monitoring well and subsoil samples from a terminal and a retail site in which MTBE was present for some time. Figure 4 shows the degradation profiles for BTEX and MTBE (ca. 3 mg/L each) in well water microcosms. No BTEX or MTBE was metabolized in test controls containing the respiration inhibitor, sodium azide. BTEX degraded rapidly ($t_{1/2} < 7$ d) in two of the three well samples (SW1 and SW3). MTBE was completely metabolized in SW1 and SW3 after a lag period of 1-3 weeks to non-detectable levels (<10 µg/L) within 3-4 weeks. Addition of the ether-degrading culture, BC-1 (20-50 mg/L), to these microcosms resulted in a rapid decline in MTBE with a $t_{1/2}$ similar to that of BTEX. Aquifer soil cores from a retail site (Ridgewood) have also shown an apparent natural decay of MTBE by indigenous ether-degrading bacteria (Figure 5). BTEX and MTBE degraded in soil/groundwater microcosms with $t_{1/2}$ of <7 and 21 days, respectively. Upon addition of 50-100 mg BC-1 cells/Kg aquifer soil, however, MTBE was rapidly degraded ($t_{1/2} < 7$ d). Very similar results were observed with seeding another aquifer soil (Southbridge) to enhance MTBE and TBA-degradation (Figure 5). In Southbridge soil samples TBA, but not MTBE, was degraded ($t_{1/2}$ 16d) by indigenous organisms present. Addition of BC-1 to the microcosm, however, reduced the $t_{1/2}$ of MTBE and TBA to 3-5d.

Saturated column flow-through experiments on the transport of BC-1 microbes through a medium grain sand were performed to (a) demonstrate that MTBE degradation can occur within a seeded core, and (b) estimate the extent of migration of ether-degraders under simulated ground water flow conditions (Figure 6). Each PVC column (1 X 48 inches) consisted of 6, 8-inch sections and was operated in a upflow mode with ground water flow rates of 4 ft/d. A control (inhibited) column contained 0.5% sodium azide to account for non-microbial mass losses during the experiment. MTBE was added to uncontaminated well water at a concentration of 3 mg/L. The first, 8 inch core section (195 g sand) was blended with 20 mg BC-1 culture (ca. 100 mg cells/Kg) and then reinserted into the column. Bromide tracer experiments confirmed the similarity of the porosity and void volume (ca. 250 ml) of each column. The results of these sand column studies are summarized in Figure 6. Effluent concentrations out of the seeded column are given only since MTBE levels were essentially the same across each of the six sample ports. This would suggest that influent MTBE was primarily degraded across the seeded sand core. Maximum MTBE removal rates (90 - 99%) in the inoculated column were observed after 20 days with effluent levels stabilizing at 0.1 - 0.3 mg/L. Little or no loss of MTBE was observed in the azide-inhibited column. After 55 days, sand core segments from the seeded column were analyzed for numbers of MTBE-degraders. A most probable number (MPN) ether-degrading assay was used (described in Figure 3) in which core material was diluted into sterile minerals and assayed for MTBE degradation after 2-3

weeks incubation. The results of the MPN assay on each column segment show the apparent distribution of ether-degraders throughout the 4 ft column with highest counts (10^3 - 10^4 /g) downgradient of the seeded core at 2-2.5 ft. This indicates that most of the inoculant was retained in the seeded core, although an approximate degrader migration rate of 0.3-ft/week was calculated for the high pore water flow-rates used in the experiment. About 10% of the original BC-1 seed culture (10^7 /g) remained in the first 0.6 ft core section and the numbers of degraders in the remainder of the sand column comprised only a small fraction (0.002%) of the total inoculated (10^8 /g). The effluent from the seeded column usually had ≤ 10 -100 ether-degraders/L. We would expect, therefore, that microbes inoculated into a aquifer soil would migrate only a short distance and also disperse/dilute into groundwater flow paths. A recent review on laboratory experiments of bacterial migration through soil media by Lawrence and Hendry⁽²²⁾ discussed how bacterial cell transport is affected by soil type, ground water flow velocity, cell morphology, hydrophobicity and charge, pH and ionic strength. Field studies of 3D modeling microbial transport in a coastal plan aquifer by De Flaun et al.⁽¹²⁾ have shown that ^{13}C -labeled bacteria migrated only 10% the flow field length from the point of injection.

In Situ Bioremediation Potential of MTBE - The Case for Aquifer Seeding

Some bioremediation scenarios that may be applicable to MTBE in ground water are given in Figure 7. In the traditional "pump and treat" technique, ground water is extracted from wells at the edge (or source area) of a plume and biotreated in an activated sludge-type or fixed film (e.g. fluidized or packed bed reactor) systems. Biotreated effluents which are below the maximum limit for the regulated chemical can be discharged to a municipal sewer or reinjected into the aquifer. Although such biotreaters can be inoculated with active ether-degrading cultures, the cost-effectiveness of consistently treating ground water constituents (BTEX and MTBE) to very low concentrations (≤ 20 $\mu\text{g/L}$) from dilute streams (low mg/L) at relatively high flow rates (10-30 gpm or higher) is not known for typical retail sites where underground gasoline tank releases have occurred. Other factors such as total loading (TPH organics), nutrient requirements for optimum biotreatment (O_2 transfer, NH_4^+ , PO_4^{3-}) and the potential for Fe^{2+} oxidation fouling also need to be considered in optimizing this remediation technology.

Our survey results (Table 3) on the presence of ether-degraders in soil and ground water show that these populations are too low and/or grow too slowly to effectively attenuate observed levels of MTBE in aquifer plumes. However, we have demonstrated that inoculation of subsoils and groundwater with ether-degrading microbes (20-200 mg cells/Kg aquifer material) can markedly shorten the $t_{1/2}$ of the oxygenate. The technique of "microbial seeding" has been used by the bioremediation industry to enhance destruction and/or transformation of organic chemicals and pesticides in soils and wastes.⁽³⁰⁾ Moreover, the success and failure of soil inoculations to stimulate degradation of poorly biotransformed compounds has been discussed by Alexander.⁽¹⁾ Such factors as survival, decay and rate of growth, adaptation, substrate/energy utilization and availability and microbial competition among existing heterotrophs influence the potential success of the introduced cultures. Bioaugmentation on a laboratory and pilot scale has been somewhat successful with remediating recalcitrant compounds such as TCE, CCl_4 , dioxins and PCP and PCB^(2,5) in which natural populations in environmental media are too low to initiate growth and/or compete with indigenous organisms for survival and maintenance energy to biotransform significant concentrations of a contaminant. Microbial cultures in the form of a biomass slurry suspension or sorbed onto a support (e.g. activated carbon, diatomaceous earth) may be injected into subsoil boreholes. Such bioimplants can be placed along the leading edge or within an MTBE plume or into source areas containing high MTBE levels. The effectiveness of ether-degrading biobarriers in an aquifer will depend upon several factors similar to those discussed for *ex situ* biotreaters such as culture decay and dilution, persistence, heterotrophic competition and long-term maintenance of metabolic activity in the soil matrix. Spacing between injection boreholes and dispersion/dilution/transport of inoculant within and outside the soil biobarrier will also be important. Finally, the ability to transport O_2 and sustain adequate dissolved O_2 levels through the barrier is critically important to the success of stimulating the aerobic bioremediation of MTBE.

<p align="center">Table 1 Properties of an MTBE-Degrading Culture (BC-1) and Ether-Degrading Systems</p>	
Feature	Characteristics
Microbial composition	Mixed bacteria (gram-positive and gram negative), pure cultures, hydrocarbon-oxidizers.
Maintenance	Continuous cell recycle reactor.
Metabolism	Strictly aerobic.
Proposed pathway	MTBE → TBA → IPA → DMK → Pyruvate → Acetate → CO ₂
Metabolites detected	Uncommon in sludges, soils and ground water.
Ethers degraded	MTBE, ETBE, TAME, DIPE, DEE, MBE
Growth rate	Low (≤ 0.05/d)
Apparent cell yield	0.1 - 0.2 g cells/g MTBE
Stoichiometry	C ₅ H ₁₂ O + 6.5O ₂ + 2NH ₃ → 0.2C ₅ H ₇ NO ₂ + CO ₂ + 5.6 H ₂ O
Substrate inhibition	Decrease in removal rate with increase in concentration.
Factors affecting growth/activity	Temp. <20°C; pH <6; DO < 1 mg/L; high loading (BOD, MTBE).
Water biotreating	Suspended solids, fixed-film, fluidized bed reactors; longer Hydraulic and biomass detention times.
MTBE effects on BTEX	Little or none (90 mg/L).
Indigenous ether-degraders (natural attenuation rate).	Uncommon or very slow adaptation/growth; ≥ 3-5 X slower than BTEX (0.001/d).
In situ aquifer bioaugmentation	Lab findings (soil/ground water microcosm inoculation).

<p align="center">Table 2 Estimated First Order Biodegradation Rates for BTEX and MTBE in Sparks Terminal Ground Water Microcosms</p>					
		Degradation rate, day ⁻¹ (lag time, days)			
		BTEX		MTBE	
Monitoring Well ^{a)}	MTBE Conc ^{b)} (ppb)	Aerobic	Anaerobic	Aerobic	Anaerobic
1	5,000 - 10,000	0.39(0)	0.01(21)	0.32(14)	0.01(28)
	25,000 - 30,000	.33(0)	.01(21)	.02(14)	<.01
	75,000 - 80,000	.34(0)	NT ^{c)}	.01(21)	NT
3	15,000 - 20,000	.09(0)	NT	.01(21)	NT
	30,000 - 35,000	.06(7)	<.01	<.01	<.01
	85,000 - 90,000	.19(14)	NT	<.01	NT
9	5,000 - 10,000	.02(14)	NT	<.01	<.01
	15,000 - 20,000	.02(14)	<.01(BEX) .09(T,21)	<.01	<.01
	55,000 - 60,000	.02(28)	NT	<.01	NT
<p>a) Numbers of BTEX-degraders in the initial well water samples were 10⁶, 10⁵, and 10⁵-10⁷ per liter for monitoring well 1, 3 and 9, respectively.</p> <p>b) Initial added MTBE concentrations in microcosm.</p> <p>c) Not tested.</p>					

<p align="center">Table 3 Survey of Environmental Samples for MTBE Biodegradation</p>			
Sample	Site (location)	MTBE Degraders^{a)}	Maximum Removal, Rate, mg/g/d^{b)}
Biosludge	Deer Park Refinery (TX)	10 ³ /g	0.48
	Deer Park Chemical Plant (TX)	10 ³ /g	.01
	Norco Refinery ^{d)} (LA)	0	ND ^{c)}
	Anacortes Refinery ^{d)} (WA)	0	ND
	Wood River Refinery ^{e)} (IL)	0	.07 - .2
	Martinez Refinery ^{e)} (CA)	ND	.16 - 1.2
Ground Water	Newport Beach - Retail (CA)	0	ND
	Bolsa Chica - Retail (CA)	0 - 10/L	ND
	Norco Refinery (LA)	0	ND
	Wood River Refinery (IL)	0	ND
	Sparks Terminal (NV)	10 - 100/L	(0.05 - 1.6 mg/L/d)
	Dayton Terminal (OH)	0	ND
	E. Hamblin Pipeline (TX)	0	0 ^{g)}
Soil/Ground Water	Mt. Clemens - Retail (MI)	0	0
	Hillcroft - Retail (TX)	0	0
	Ridgewood - Retail (NJ)	ND	.00057(0.28 mg/L/d)
MTBE Cultures			
BC-1		10 ³ /mg	24-168
BC-3		3X10 ⁴ /mg	90-300
Rutgers		ND	50 ^{g)}
<p>a) MTBE degraders were assayed in sludges, groundwater (1L amount) and subsoils by a most probable no serial dilution (1:10) to extinction in Bushnell-Haas (Difco) minerals containing 1 mg/L MTBE. Values are numbers of degraders per g dry wt cells or per L ground water.</p> <p>b) Calculated using a computer program that fits a first-order decay of the data; mg MTBE/g dry wt cells/day (sludges) or mg MMTBE/L/day (ground water) or mg MTBE/g soil/day (subsoil). Comparable rates of removal for BTEX in 1) different subsoils varies from 0.001 - 0/m/g/d with zero-order or pseudo-first order decays, and 2) refinery activated sludges is in the range of 24-280 mg/g cells/d based on substrate saturation (Monod-type) kinetics.</p> <p>c) ND, not done.</p> <p>d) MTBE not present in biotreater primary effluent.</p> <p>e) MTBE preent in biotreater primary effluent (≤20-45 mg/L).</p> <p>f) Samples in which no MTBE-degrading activity was observed were incubated for 4-6 weeks.</p> <p>g) Data from reference 11.</p>			

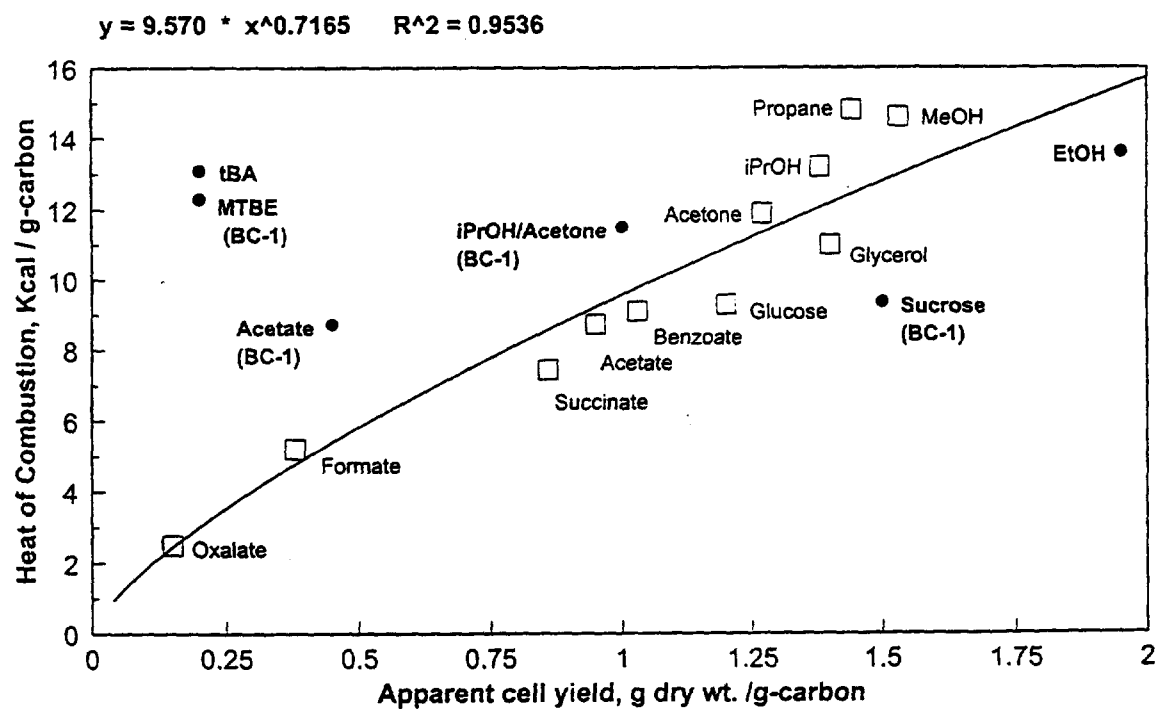
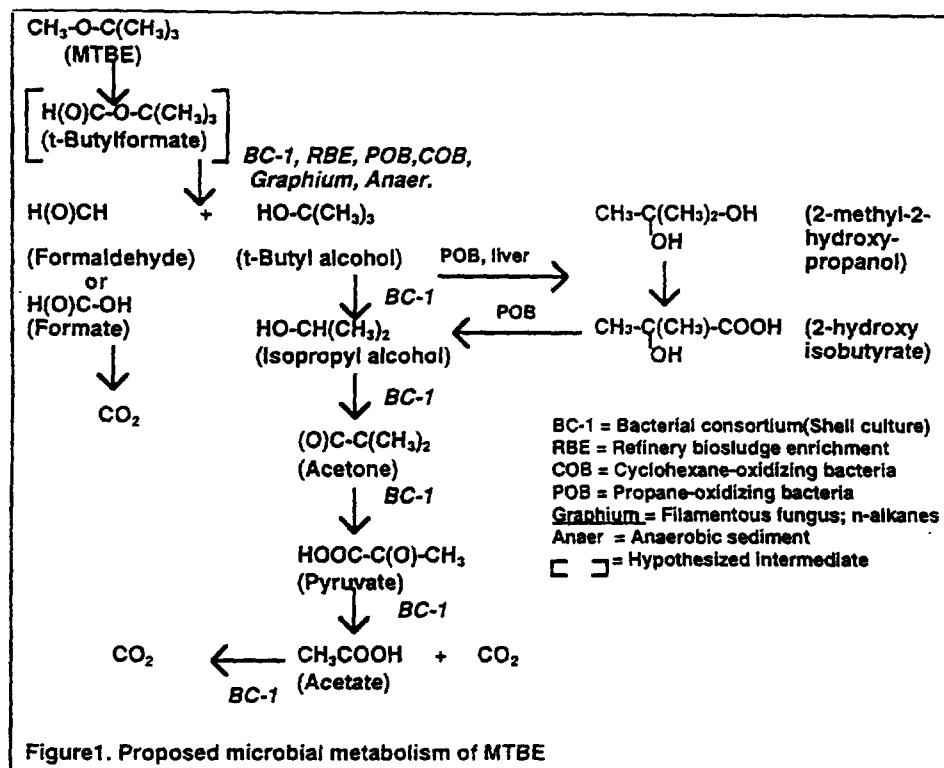
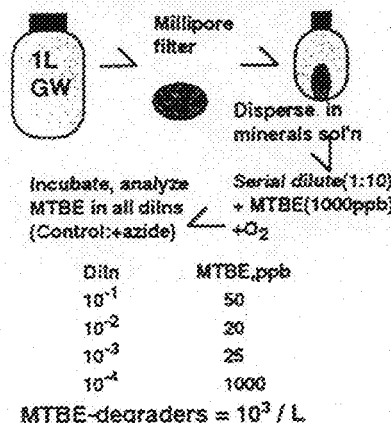


Figure 2. Substrate heats of combustion and bacterial cell growth

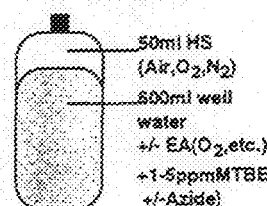
Extinction Dilution Method (MTBE-Degraders)



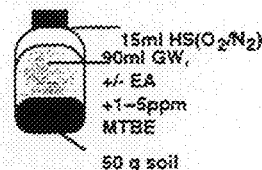
Soil Samples (2-10g): Serial dilute (1:10) in minerals sol'n

Experimental Microcosms Aerobic / Anaerobic (Serum Bottle)

Ground water



Soil / Ground water



Sampling: MTBE, HS gases, dissolved EA

Figure 3. Serum bottle assay systems for MTBE biodegradation

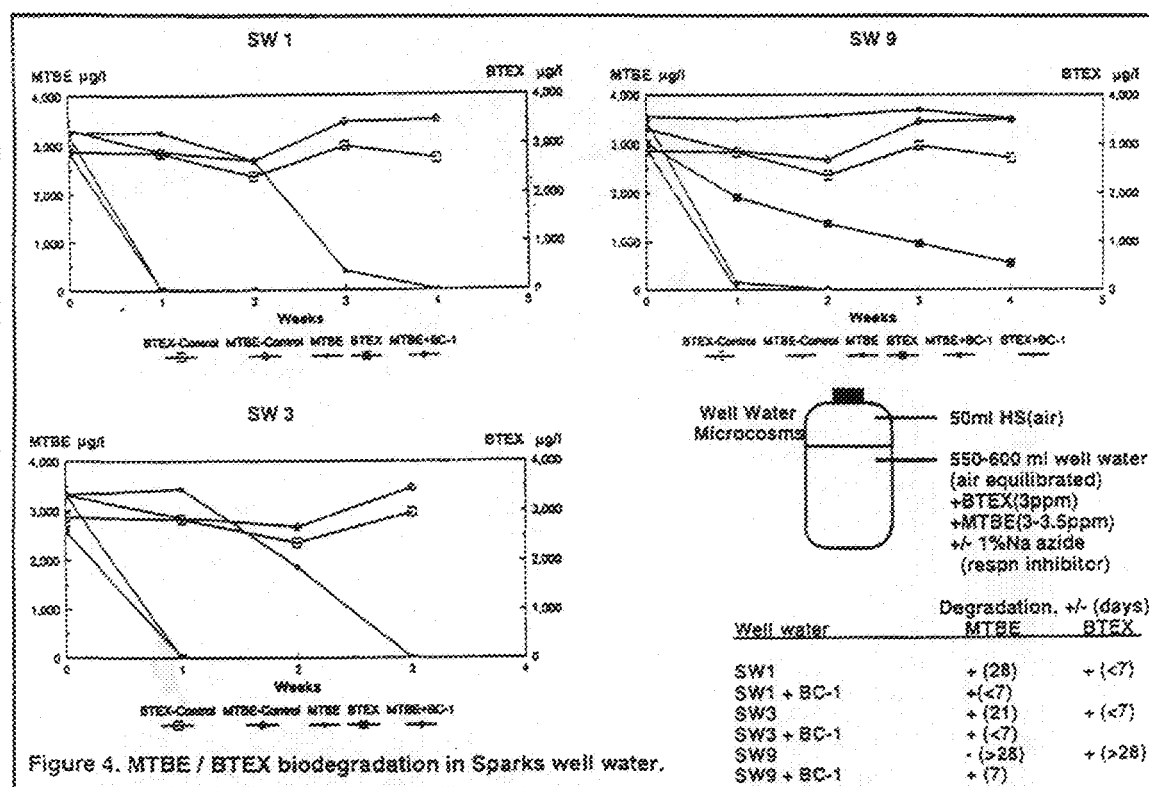
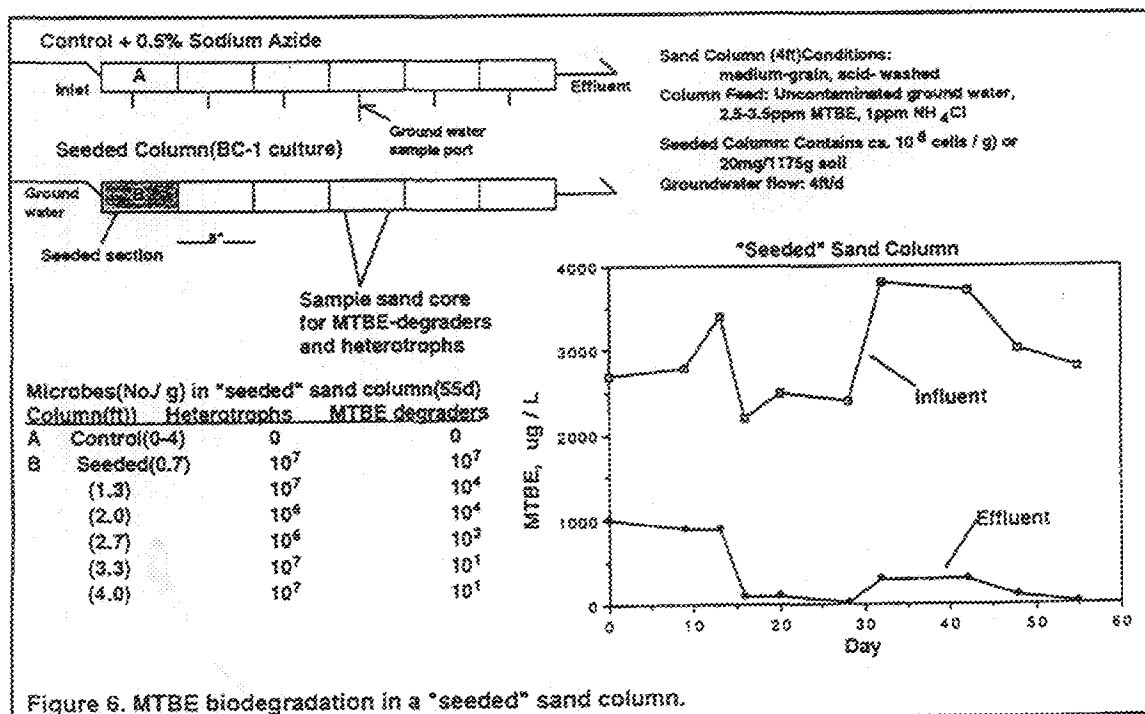
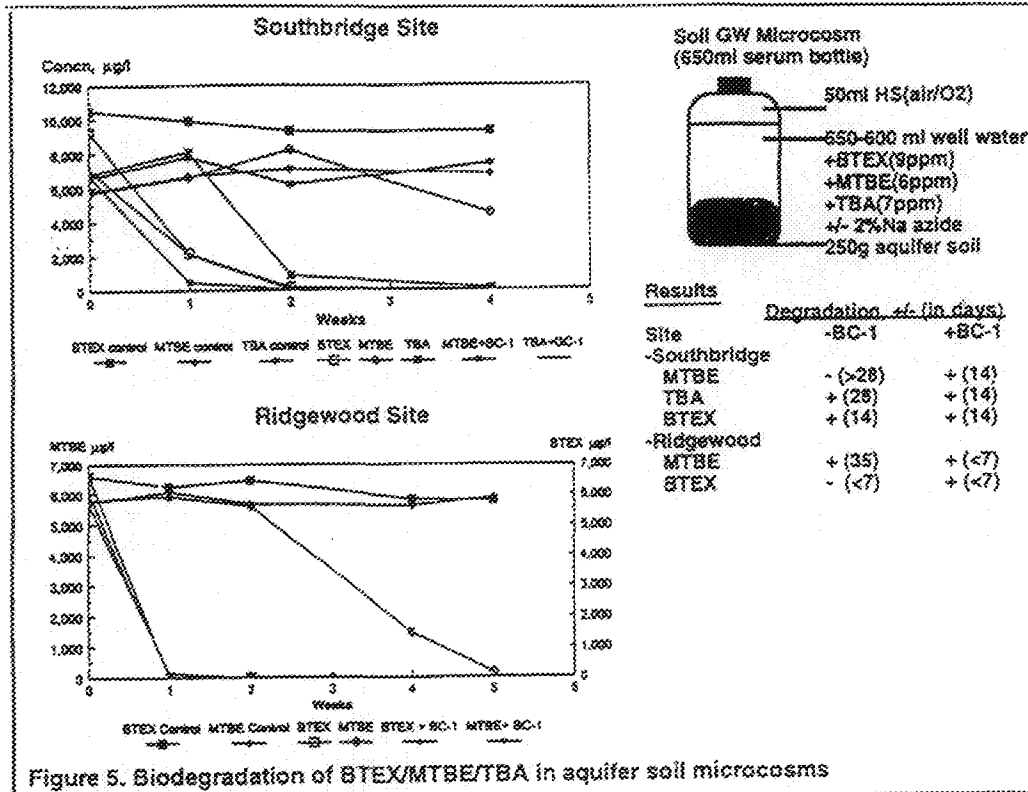


Figure 4. MTBE / BTEX biodegradation in Sparks well water.

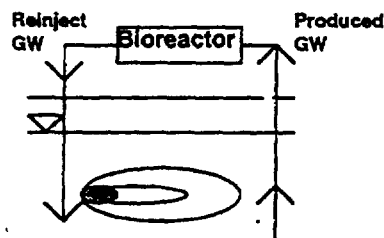


BTEX / MTBE Plumes

BTEX MTBE



"Pump and Biotreat"



Treatment Factors:

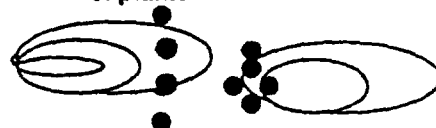
- *Remove GW vs. flushing source
- *Flow rate(gpm) / residence time in reactor
- *Growth / stability of culture
- *BTEX / MTBE concns.(infl/effl)
- *O₂ transfer
- *Fe⁺² fouling

Natural Attenuation Significance

- Monitor wells for decrease in MTBE/BTEX
- Shrinking, stable, expanding plumes
- MTBE moves with GW
- Little retardation
- MTBE plumes separate from BTEX plumes(biodeg'n slower than GW)
- How to enhance naturally-occurring degraders(cosubstrates?)

Microbial "Seeding" of Subsoil

Leading edge of plume Source treatment



- = Bioimplant of MTBE - degrading microbes(free/immobilized)

Treatment factors:

- *Growth/stability/decay of "seed"
- *Nutrient requirements(O₂,N)
- *BTEX(TPH) / MTBE levels
- *Transport/dilution of "seed"

Figure 7. Bioremediation options for treatment of MTBE in ground water

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MTBE Biodegradation in the Presence of Other Gasoline Components

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Abstract

A microbial culture degrading MTBE was tested for its ability to degrade additional fuel oxygenates and gasoline components. The fuel oxygenates considered were TAME, DIPE, and ETBE, and the gasoline components included benzene, toluene, *n*-hexane and methylcyclopentane. The experiments were conducted in batch liquid culture with MTBE being introduced in combination with each of the other contaminants. Another objective of the experiments was to investigate the effect of the presence of the additional contaminant on MTBE biodegradation. Results showed that the microbial culture was able to degrade TAME, benzene and toluene with little or no effect on MTBE biodegradation. The culture was not able to degrade the other contaminants however, and the presence of those contaminants had no effect on MTBE degradation. A separate experiment was then conducted to investigate the ability of the culture to biodegrade and grow on toluene (a more easily degradable carbon source), and yet maintain its ability to degrade MTBE. Samples of the MTBE-degrading culture were fed toluene only, for different amounts of time (up to 4 weeks), and then switched back to MTBE only. The cultures were able to degrade MTBE once it was introduced again with little or no lag.

Introduction

A few reports have been published addressing aerobic biodegradation of methyl tertiary butyl ether (MTBE) under controlled laboratory conditions (Salanitro *et al.*, 1994; Cowan and Park, 1996; Park and Cowan, 1997; Mo *et al.*, 1997; Steffan *et al.*, 1997). Fewer reports have been published however, on the biodegradability of MTBE in the presence of more easily degradable substrates, or on the biodegradability of other fuel oxygenates. Mo *et al.*, (1997) examined the ability of two pure cultures to degrade MTBE when combined with either tertiary butanol, butyl formate, isopropanol, acetone, or pyruvate. In all cases, less MTBE was biodegraded when combined with another carbon source, as compared to the control which contained MTBE alone. Cowan and Park (1996) used a MTBE enrichment culture derived from petroleum refinery wastewater activated sludge to further enrich and acclimate for the fuel oxygenates tert-amyl methyl ether (TAME), ethyl tert-butyl ether (ETBE), and tertiary butyl alcohol (TBA). Several mixed cultures were obtained each capable of using one of those oxygenates as a single carbon and energy source. Steffan *et al.*, (1997) reported biodegradation of MTBE, TAME and ETBE by bacterial strains grown on propane. The bacteria could not use the oxygenates as growth substrates.

In this study, a mixed microbial culture growing on MTBE was examined for its ability to degrade other fuel oxygenates and gasoline components. The culture was initially derived from a compost-based biofilter, degrading MTBE, at the Joint Water Pollution Control Plant of the Los Angeles County Sanitation Districts (Eweis *et al.*, 1997). It was grown in batch liquid culture, under controlled laboratory conditions, using MTBE as the single carbon and energy source. Plating indicated the presence of at least 6 different colony morphologies within the mixed culture. More microbiological work is currently underway to examine culture identities and identify any pure culture(s) capable of using MTBE as a single carbon and energy source (Hanson *et al.*, 1998).

Three, ether-based fuel oxygenates, were considered: TAME ($\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3$), ETBE ($(\text{CH}_3)_3\text{COCH}_2\text{CH}_3$), and diisopropyl ether (DIPE, $(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$). Several gasoline components were also considered: benzene and toluene were chosen as examples of aromatics (toluene for being the more easily biodegradable of the BTEX group, and benzene for its toxicity). *n*-hexane was chosen as an example of an

alkane, and methylcyclopentane (MCP, $C_5H_9CH_3$) as an example of a cyclic compound. The main objective of this work was to investigate the ability of the MTBE-degrading culture to biodegrade other contaminants, including fuel oxygenates and gasoline components, as well as to examine the effect (e.g., substrate competition, or inhibition) that the presence of these contaminants may have on MTBE biodegradation.

Materials and Methods

All chemicals (TAME 94%, ETBE 97%, DIPE 99+%, toluene 99.8%, benzene > 99%, n-hexane 99.5%, and MCP 99+%) were purchased from Fisher Scientific, and Acros Organics (a division of Fisher Scientific). The experiments to study MTBE degradability in the presence of other organic contaminants were conducted in three phases, with toluene and benzene each considered separately. Table 1 summarizes the experimental setup for each phase, including the initial concentration of contaminants. A separate experiment was also conducted to study the ability of the culture to degrade MTBE after it had been exposed to toluene for some time. Bottles were prepared in sets of two and fed only toluene for various amounts of time before being switched back to MTBE. All experiments were conducted in 250 ml amber glass bottles, each containing 30 ml of an autoclaved phosphate buffered mineral salts solution (Eweis *et al.*, 1997). The same amount of inoculum (the MTBE-degrading mixed culture) was added to all bottles, within each set of experiments, except for the control which received no inoculum. The bottles were sealed with Teflon-lined caps, equipped with septa and open/close valves, to allow for gas sampling from the headspace. Bottles were incubated on a horizontal shaker at temperature ranging between 21 and 23 °C. Substrate disappearance was monitored by sampling the gas phase. Gas samples were collected using 5 ml gas-tight syringes equipped with Teflon Mininert® valve fittings. Samples were analyzed using a Shimadzu 14A gas chromatograph (GC) equipped with a 0.5 ml gas sample loop and a flame ionization detector (FID).

Results and Discussion

Degradation of MTBE in the presence of a low (5 ppm) and high (20 ppm) toluene concentration can be seen in Figure 1(a). The presence of toluene, a more easily degradable substrate, did not have a negative effect on MTBE degradation. The results are suggestive of better removal in the presence of a high concentration of toluene, as compared to MTBE alone. However, given that only one bottle was used with MTBE alone, there is not enough statistical evidence to indicate that the results are significantly different. The degradation of toluene in the presence and absence of MTBE is seen in Figure 1(b). The MTBE degrading culture degraded toluene relatively quickly (for the same cell concentration, 20 mg/l of toluene were degraded in 2 to 3 days while 10 mg/l of MTBE were degraded in 4 days). Similar results were obtained with benzene (Figure 2). The presence of benzene in combination with MTBE did not negatively influence MTBE degradation, and the culture was also able to degrade benzene at a rate faster than MTBE degradation.

The results of MTBE degradation in the presence of the other gasoline components and fuel oxygenates are shown in Figure 3. Although DIPE, ETBE, hexane and MCP were not biodegraded, their presence in combination with MTBE did not significantly affect MTBE degradation (Figure 3(a)). TAME was the only fuel oxygenate that was degraded (Figure 3 (b)). The rates of degradation of TAME and MTBE were similar (Figure 3(c)). The rate of MTBE degradation in the presence of TAME may appear to be slower than MTBE degradation in the presence of the other contaminants (Figure 3(a)). That is not necessarily true however, considering that on a cell mass basis, there was approximately twice as much carbon biodegraded in the case of MTBE/TAME combined, compared to the other sets where only MTBE was degraded. The fact that TAME was the only other ether that was degraded suggests that the initial enzymatic attack occurs at the oxygen-methyl bond, which is common to both MTBE ($CH_3OC(CH_3)_3$), and TAME ($CH_3CH_2C(CH_3)_2OCH_3$). That might explain why ETBE ($CH_3)_3COCH_2CH_3$) and DIPE ($CH_3)_2CHOCH(CH_3)_2$) were not degraded. Cowan and Park (1996) reported degradation of both TAME and ETBE (DIPE was not included in that study) by mixed microbial cultures derived from a MTBE enrichment culture. There was no mention however of whether one culture was able to degrade both compounds, or whether the MTBE-degrading culture was able to

degrade the other two oxygenates. Since the species identities within the mixed cultures were not examined, it is also unclear how different (or how similar) the different enrichment cultures were.

Results of the experiment investigating the ability of the culture to degrade MTBE, after it had been exposed to toluene for varying amounts of time, are shown in Figure 4. The culture was fed only toluene for 3, 4, 5, and 6 days (Figures 4 (a), (b), (c), and (d) respectively) before MTBE was reintroduced as the only carbon source. In each case, the culture was able to degrade MTBE again with little or no lag. Two more sets of bottles were fed toluene for 11 and 28 days respectively before reintroducing MTBE and the same results were observed (data not shown). Although MTBE biodegradation is slower than toluene degradation, the fact that the same mixed culture was able to degrade MTBE after long exposure to a more easily biodegradable substrate is encouraging when considering practical applications. It is unclear however, whether the same organisms are responsible for degrading both compounds, or if the enzymatic pathways are similar. Some of these issues will be addressed in future studies.

Conclusions

In all of the experiments conducted, the presence of an organic contaminant in combination with MTBE did not negatively influence MTBE degradation. The MTBE-degrading culture was able to degrade TAME, toluene and benzene, but not the other compounds included in the study. The culture degraded toluene and benzene at a rate faster than MTBE degradation. The biodegradation of TAME however, was at a rate similar to that of MTBE. The culture was also able to degrade toluene for long periods of time without losing its ability to degrade MTBE.

The results obtained from this work are important for practical applications where the MTBE-degrading culture may be used in a biological treatment process. Given that MTBE is a gasoline additive, it is likely that it will elute with other contaminants that are components of gasoline. Although MTBE may eventually distance itself from other components, the ability of the culture to degrade other organic compounds, while maintaining its capacity at degrading the target compound, is an important indicator of culture robustness and hence process stability. At the same time, the fact that the MTBE degrading culture is unable to degrade some other organic compounds, although not surprising, is important for process design. Experiments are underway to determine whether the culture can co-exist with other cultures that are known to degrade gasoline components such as hexane

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Table 1: Summary of setup for experiments involving MTBE degradation in the presence of other organic contaminants.

Contaminant other than MTBE	Number of replicas (bottles)	Contaminant (initial concentration mg/l)
Toluene	3 3 1 1 1 1 (control)	MTBE (10) + toluene (5) MTBE (10) + toluene (20) Toluene (5) Toluene (20) MTBE (10) MTBE (10)
Benzene	3 3 3 1 (control)	MTBE (40) + benzene (20) MTBE (40) Benzene (20) MTBE (40) + benzene (20)
TAME, ETBE, DIPE, MCP, and n-hexane	2 2 2 2 2 2 2 (control)	MTBE (30) + TAME (30) MTBE (30) + ETBE (30) MTBE (30) + DIPE (30) MTBE (30) + MCP (30) MTBE (30) + n-hexane (30) MTBE (30) MTBE + all other contaminants each at 30 mg/l

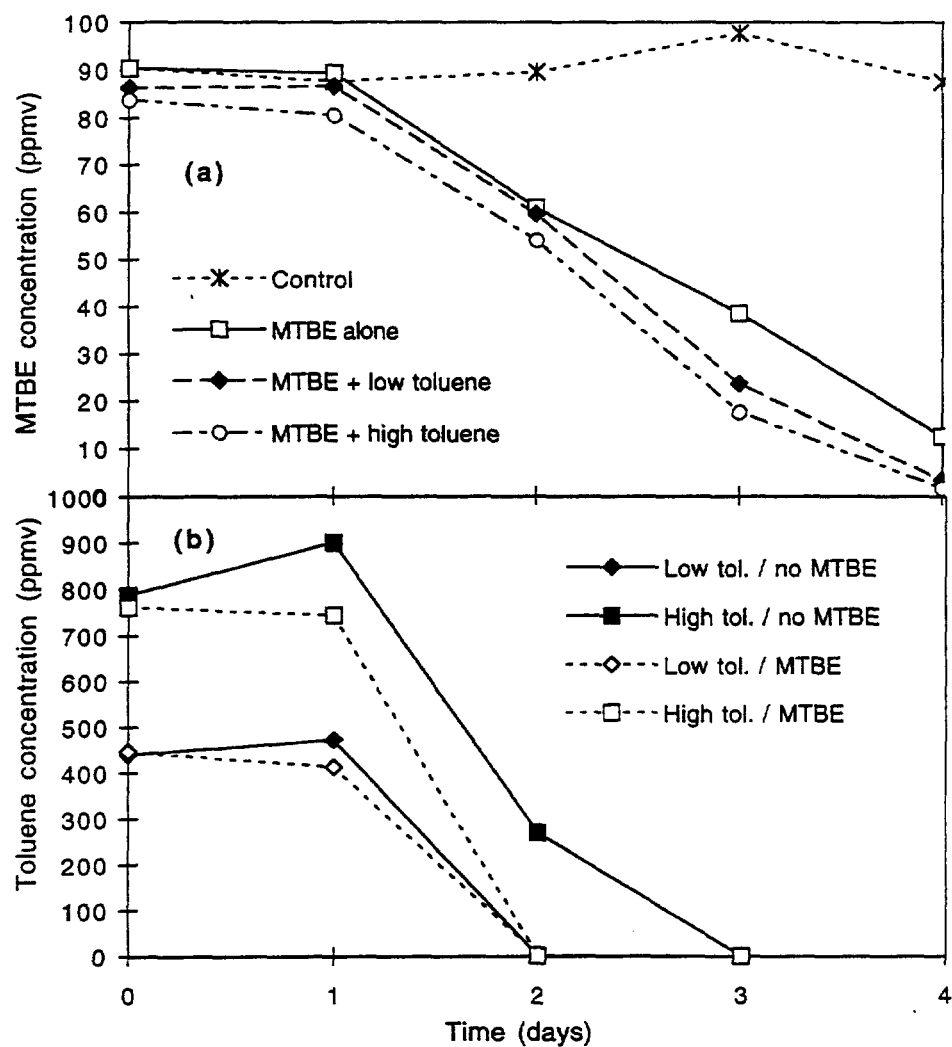


Figure 1: MTBE removal in the presence and absence of toluene (a), and toluene removal in the presence and absence of MTBE (b). Concentrations are in parts per million on a volume basis measured in the headspace.

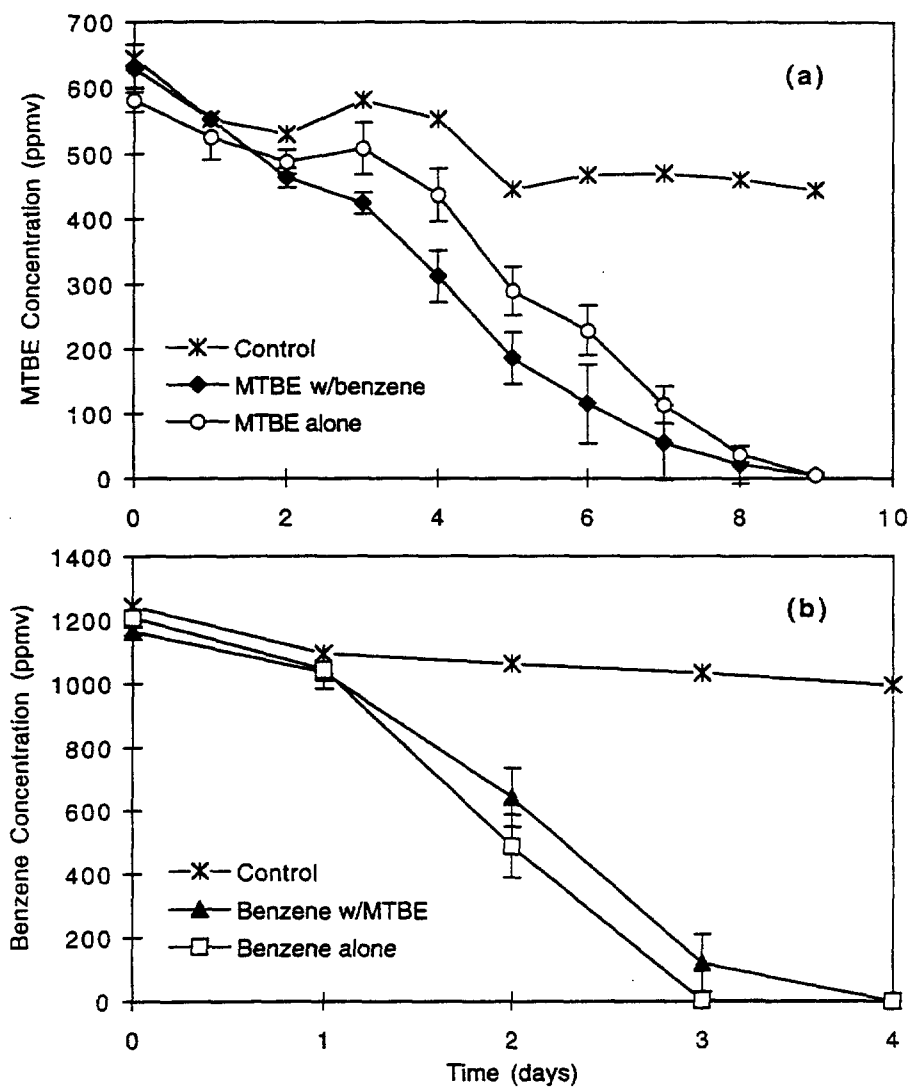


Figure 2: MTBE removal in the presence and absence of benzene (a), and benzene removal in the presence and absence of MTBE, (b). Error bars are based on one standard deviation from the mean.

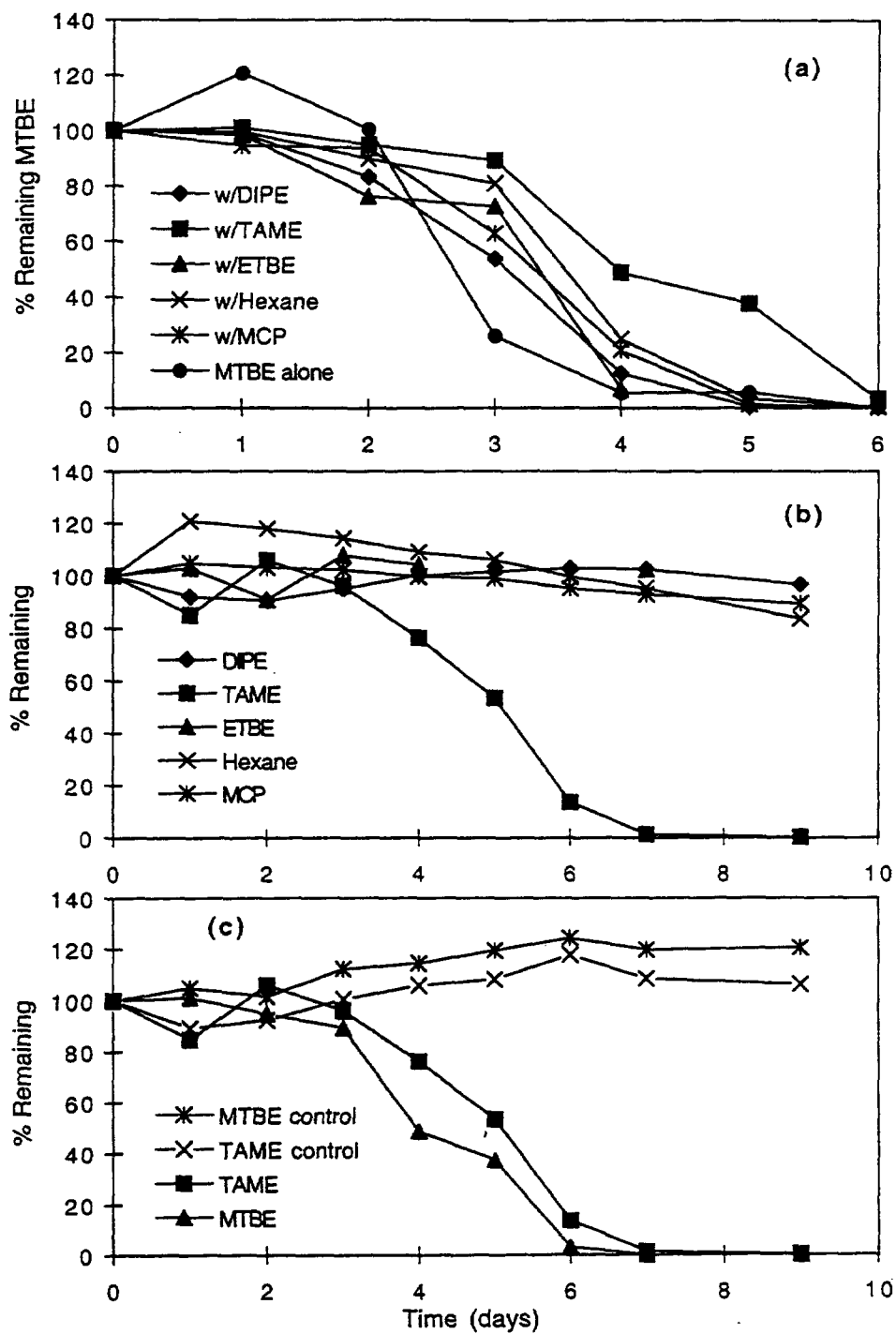


Figure 3: MTBE removal in presence of other contaminants (a), and removal of other contaminants in presence of MTBE (b); (c) shows TAME and MTBE removal occurring in the same bottles. Each data point is the average of two bottle readings.

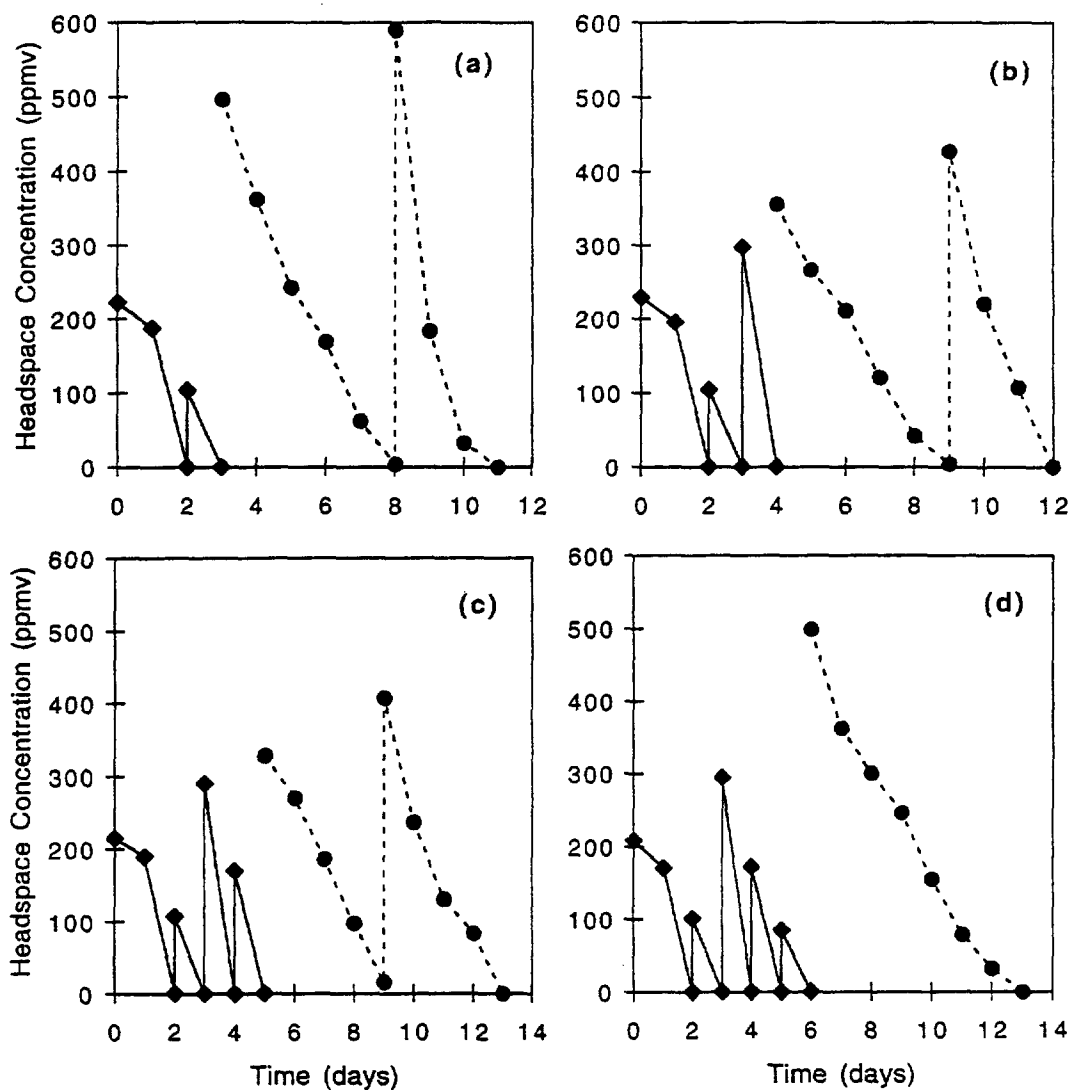


Figure 4: Removal of MTBE (●) after exposure to toluene (◆) for 3 days (a), 4 days (b), 5 days (c) and 6 days (d). Each data point is the average of two bottle readings. Discontinuities in the graphs indicate times when chemical additions were made after the contaminant was consumed

Important Ecological Risk Assessment Parameters for MTBE and Other Gasoline Oxygenates

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Abstract: Alcohols and ethers may be used in modern gasolines for a variety of purposes. Methyl tertiary-butyl ether (MTBE) is the most commonly used motor fuel oxygenate and may be found in gasoline at concentrations as high as 15% by volume, in some areas of the United States. Although risk-based corrective action (RBCA) decision-making at gasoline release sites often focuses on human health analyses, there are release scenarios where ecological risk assessment may be required. Physicochemical data for ethers and alcohols are sufficiently well understood to generally predict their behavior and fate in environmental media. Ecotoxicological "effect" data, however, are somewhat less accessible in the technical literature and may be difficult to apply for site-specific ecological risk assessments. A variety of toxicity reference values for use in ecological risk assessment are provided here for aquatic and selected terrestrial biota. MTBE concentrations below 66 mg/l in freshwater habitats and less than 8 mg/l in marine systems would not be anticipated to cause adverse ecological effects. Additional, freshwater aquatic toxicity reference values, calculated as "maximum acceptable toxicant concentrations", for other ethers and alcohols range from 27 mg/l to 914 mg/l. No adverse effects on small mammals would be expected from atmospheric MTBE concentrations of 250 ppmv or less. Soil concentrations of MTBE as high as 1250 mg/kg would not be expected to cause adverse effects as a result of soil ingestion by mammals. Worst-case dermal exposure assumptions indicate that a soil concentration of 500 mg/kg MTBE would not cause adverse effects on small, burrowing mammals. These toxicity reference values may be used for a variety of quantitative ecological risk assessment purposes.

Introduction

Low carbon number ethers and alcohols are used for a variety of purposes in modern gasolines. Although methyl tertiary-butyl ether (MTBE) is the most widely used oxygenate, others are available and are identified in Tables 1 & 4. Important, predictive parameters of environmental fate and behavior in environmental media are presented in Table 1. When such information is used in combination with empirical, site-specific concentration data and appropriate toxicity reference values, quantitative risk assessments can be

conducted. Human health risk assessments are often conducted at gasoline spill/release sites for risk-based decision-making purposes. Ecological risk assessments, although less frequently indicated at release sites, require toxicity reference values which are problematic to locate or develop from the existing literature. Relevant toxicity reference values are presented here.

Discussion

MTBE aquatic toxicity data for a variety of freshwater and marine species are summarized and presented in Table 2. Existing data indicate that MTBE exhibits a low level of aquatic toxicity, expressed by nonspecific narcosis and has a low potential for bioaccumulation (Mancini, 1997). Based upon these existing data, aquatic toxicity reference values were calculated (Table 3). These reference values were calculated by generally following the guidance for developing federal ambient water quality criteria (USEPA, 1985).

Additional freshwater toxicity reference values for other alcohols and ethers are presented in Table 4. These "maximum acceptable toxicant concentration" values were calculated based upon quantitative, structure-activity relationship predictions of chronic (sublethal) effects to the fathead minnow (*Pimephales promelas*). The Table 2, 3 and 4 data may be used with both predictive models as well as site-specific water quality data for conducting aquatic ecological risk assessments. Ecological risk assessments for several spill/release scenarios, including groundwater plume discharges to gaining stream reaches, will be presented.

A variety of mammalian toxicological data have been summarized by Brown (1998) and provide a basis for calculating toxicity reference values for fossorial (underground dwelling) mammals via three potential routes of MTBE exposure: dietary, dermal and inhalation. Since MTBE demonstrates a low potential for bioaccumulation (Fujiwara, *et al.*, 1984), the greatest dietary exposure is expected to result from incidental soil ingestion. Through the use of published soil ingestion rates (Beyer, *et al.*, 1994) and relevant quantitative risk calculations (Sample, *et al.*, 1996), the no-effect MTBE soil concentration was determined to be 1250 mg/kg. A conservative estimate of the no-effect concentration of MTBE in soil for a dermal exposure route for small mammals was calculated to be approximately 500 mg/kg. The no-effect concentration for an inhalation exposure route is approximately 250 ppmv, as determined directly through laboratory inhalation studies.

It is intended that these toxicity reference values be used in conducting generic as well as site-specific ecological risk assessments, and for rapid reference purposes during emergency response operations.

Table 1. Physicochemical characteristics and environmental fate parameters for selected alcohols and ethers.

Parameter	MTBE	TAME	ETBE	Methanol	Ethanol	TBA
Mol. wt. (g/mol)	88	102	102	32	46	74
Vapor press. (mm Hg)	245	75	130	92	45	40
Density (g/ml)	0.74	0.77	0.74	0.80	0.79	0.79
Neat Solubility (mg/l)	46,000	12,000	12,000	*	580,000	100,000
Henry's Constant (dimension- less)	0.040	0.080	0.100	0.0002	0.0003	0.001

*- miscible

Table 2. Summary of acute and chronic exposure aquatic toxicity data for MTBE.

Organism/Exposure	EC ₅₀ /LC ₅₀ (mg/l)
Freshwater/acute	
Green alga	195
Water flea	340-681
Fathead minnow	672-980
Rainbow trout	887
Frog	2500
Freshwater/chronic	
Water flea	203 (IC ₂₅)*
Fathead minnow	234 (IC ₂₅)
Marine/acute	
Copepod	>1000
Mysid shrimp	44-136
Silverside minnow	606
Bleak	>1000
Sheepshead minnow	>2500

*- IC₂₅ is the concentration estimated to cause a 25% reduction in organism performance relative to control

Table 3. Recommended aquatic toxicity reference values for MTBE.

Water Quality Objective	Concentration (mg/l)
Freshwater	
Acute effects protection	115
Chronic effects protection	66
Marine	
Acute effects protection	14
Chronic effects protection	8

Table 4. Freshwater toxicity reference values (mg/l) for selected alcohols, ethers and benzene. *Based upon quantitative, structure-activity relationship predictions of chronic effects to the fathead minnow; may be used as maximum acceptable toxicant concentrations for ecological risk assessment purposes.*

Compound	Toxicity Reference Value (mg/l)
Benzene	7
Ethyl tertiary-butyl ether (ETBE)	27
Tertiary-amyl methyl ether (TAME)	27
Diisopropyl ether (DIPE)	32
Methyl tertiary-butyl ether (MTBE)	66
Tertiary-butyl alcohol (TBA)	177
Ethanol	455
Methanol	914

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Public Health Implications of MtBE and Perchlorate In Water: Risk Management Decisions For Water Purveyors

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Recent public health debates on water quality have focused on the detection of chemicals in drinking water supplies and not on the risk management decisions for water purveyors who will have to sell water containing trace amounts of these chemicals. Unlike Dr. John Snow who reduced Asiatic Cholera in London in the 1850s by removing the pump handle from the St. James Parish well, many of the new contaminants found in water today may take decades of exposure before measurable health effects manifest themselves. Although scientists have become adept at measuring the responses of isolated cellular systems to these chemicals in flasks and test tubes, moral and ethical prohibitions on experiments with humans has forced public health officials to rely on surrogate (cellular and animal) systems to define "safe" concentrations of chemicals for humans.

Two chemicals whose presence in drinking water supplies are currently being debated are the fuel oxygenate methyl *tertiary* butyl ether (MtBE) and the solid rocket fuel ammonium perchlorate (perchlorate). Both chemicals are known to be very hydrophilic and may have significant health effects associated with their presence in drinking water, yet they have been accidentally introduced into public drinking water supplies. These two chemicals symbolize the growing issue of risk management facing water purveyors today.

This discussion will investigate the risk communication issues facing the water purveyors. Topics will include:

- Identifying and engaging stakeholders from both sides of the issue;
- Addressing the public's concern for "pure water";
- Educating the public on the use of water containing residual amounts of chemicals; and
- Reintroducing the Public Health Approach Into the Risk Management Process - Framing future debates on the social and economic costs of MtBE and perchlorate to water supplies.

Identifying and engaging stakeholders from both sides of the MtBE and perchlorate issues

Who is effected by the presence of unwanted chemicals in drinking water supplies (Stakeholders in the issue)? Does every stakeholder need to be involved in the process? What are the critical elements which each stakeholder needs to be involved with? Who drives the process to a satisfactory conclusion? Will the public's health be protected? What natural resources will be adversely affected? These are the questions which drive the risk management process and ultimately decide public health policy.

Stakeholders include the public served the water, purveyors of water, the regulatory community, and producers/users of the chemicals of interest. Involvement of stakeholders left out of previous communications is essential, particularly the public, who are most often left out of the debate over chemicals in drinking water supplies. Since the introduction of public health services in the 1700's to control the spread of communicable diseases, governmental agencies, such as local Public Health Departments and more recently the Environmental Protection Agencies, have served as "caretakers" of the public well being, relieving the public of the responsibility of reviewing scientific data and deciding policy. With millions of chemicals having been formulated since the turn of the century and many more on the way, regulators are generally unable to act proactively and tend to react after the inadvertent release of chemicals to the environment. As a result water purveyors were then handed mandates by the regulatory agencies to meet guidelines meant to protect the public.

To date, a thorough debate involving all of the stakeholders on the presence of residual amounts of these chemicals in the water supplies has yet to proceed. Several stakeholders in the process, the regulatory community and the producers and users of the chemicals, are the only active participants in the debate. Although early legislation, such as the National Environmental Protection Act of 1969 (NEPA) and the Resource Conservation and Recovery Act of 1976 (RCRA or Superfund), and mandates from regulatory bodies, such as federal and local EPAs, appeared to provide a comprehensive network of legislation for protecting the environment and the public health, the public was subsequently informed by the media that environmental problems were not being resolved. Reports of up to ninety cents of every dollar being spent on environmental enforcement actions going to attorney's fees has left the public feeling that the legislation passed and regulatory bodies in place are impotent. The rise of single issue public advocacy groups and toxic tort claims either under CERCLA actions or under local laws concerning public nuisance, trespass, or contract claims, appeared to be public's only entry into the debate.

With the maturation of environmental legislation and regulatory policy, a recent shift towards source assessment and protection programs has occurred. These policies are typically based on risk management decisions which require the delineation and protection of seriously impaired resources. Victor Cohn notedⁱ that while risk may be perceived by environmental professionals as "some kind of multiplication of probability (how often does it happen) times magnitude (how bad is it when it happens)" ... "for the rest of society ... mortality matters", and the public is not as sanguine when involuntarily confronted with risk. While the public is known to be willing to accept concentrations of chemicals it perceives as natural or non-threatening, such as chlorides and nitrates, chemicals such as M/BE and perchlorate, which are seen as unnatural and harmful, are immediately perceived in a negative fashion by the public no matter what the concentration of M/BE or perchlorate. Cohn further notes that the public has become "chemophobic" and "cancerphobic".ⁱⁱ New source water protection policies are attempting to increase public involvement through the use of State Water Assessment Programs, which require Water Purveyors, a large stakeholder in the issue, to inform and educate the public, through water quality and consumer confidence reports., while trying to sell a product which they may perceive as being "polluted."

Members involved in the debate need to be reminded of the USEPA's Cardinal Rules of Risk Communicationⁱⁱⁱ which provide the clearest guidelines for communicating with all stakeholders. The Cardinal Rules include:

1. Accept and Involve the Public as a Legitimate Partner
"Demonstrate your respect for the public and your sincerity by involving the community early, before important decisions are made."
2. Plan Carefully and Evaluate Performance
"Begin with clear, explicit objectives - such as providing information to the public, motivating individuals to act, stimulating emergency response, or contributing to conflict resolution."
3. Listen to Your Audience
"Communication is a two-way activity."
4. Be Honest, Frank, and Open
"In communicating risk information, trust and credibility are your most precious assets."
5. Coordinate and Collaborate with Other Credible Sources
"Few things make risk communication more difficult than conflicts or public disagreement with other credible sources."
6. Meet the Needs of the Media
"The media are major transmitters of information on risks.... The media generally are more interested in politics than risk, simplicity than complexity, and danger than safety."
7. Speak Clearly and with Compassion
"Technical language and jargon are useful as professional shorthand. But they are barriers to successful communication with the public."

Addressing the public's concern for "pure water"

Increased public awareness regarding the benefits of clean water has resulted in promulgation of a national water quality standard, in the form of the Safe Drinking Water Act (SDWA), enacted in 1974 and amended in 1982 and 1996. The SDWA authorized the Environmental Protection Agency (EPA) to regulate public drinking water system contaminants. This Act significantly expanded Federal authority over drinking water by making the EPA responsible for establishing national standards for contamination levels in public drinking water systems, underground injection wells, and sole source aquifers. While mandating national standards created a fairly homogeneous water supply in the United States and increased public confidence in the water supplies, most water quality issues today are best dealt with on a local level.

In response to the issue of MtBE in water supplies, California law-makers have taken the lead in promulgating legislation designed to protect public water supplies and health. Three specific bills have been introduced which are designed to protect water supplies, assist in the recovery of clean-up costs, and to track contamination throughout the state. The Cunneen Bill (AB 1491) seeks to ensure that all underground storage tanks (USTs) will meet 1998 standards (double wall construction) to receive shipments of gasoline. The MtBE Public Health and Environmental Protection Act (SB 521 introduced by Senator Mountjoy) requires further studies on the health effects of MtBE, evaluation of treatment technologies, and compatibility studies of MtBE and fiberglass UST systems. The bill also requires the Governor of California to certify by January 1999 whether MtBE poses a risk to human health and the environment, and to take appropriate action if necessary. SB 521 requires testing of soil and groundwater before closure of UST sites, and the clean-up of any MtBE spill that poses a threat to drinking water sources. In addition, public drinking water systems are not responsible for the cost of treating or cleaning-up contamination, and the bill authorizes the system to recover the costs from responsible parties (RPs) and other funding agencies. The final portion of the bill allows the costs of clean-ups to be passed onto water consumers if necessary. The Local Drinking Water Protection Act of 1997 (SB 592 introduced by Assembly Person Kuehl) seeks to have the California Department of Health Services (DHS) develop a secondary drinking water standard by July 1998 and a primary standard by July 1999. The bill includes a provision for a GIS database pilot study of the Santa Monica and Santa Clara basins indicating the location and types of pipelines, USTs, drinking water wells, and hydrogeologic factors. The GIS database is to be funded by the California UST Clean-up Fund.. SB 592 further requires that a database of pipelines within 1000 feet of drinking water wells be developed, a Pipeline Safety Advisory Board be formed, and that pipeline operators prepare well protection plans. The Kuehl Bill also requires the California Regional Water Quality Control Board (CRWQCB) to notify public water systems that may be impacted by MtBE. The Bill ensures that public drinking water systems have the same legal rights as landowners to seek remedies from RPs and allows them to seek reimbursement for treatment or alternative water supplies through the UST Clean-up Fund. Finally, the Bill requires a Proposition 65 determination on the potential for MtBE to cause adverse health effects.

Educating the public on the use of water containing residual amounts of chemicals

As stated earlier, in the case of MtBE, risk communication thus far has been a war of words between pro- and anti-MtBE forces. This war has been waged in the media using a series of conflicting toxicological reports, many based on animal toxicological studies, and anecdotal evidence, based on the exposures of individuals to MtBE vapors. In some instances consumers are being told the issue comes down to a battle over clean air versus clean water. For perchlorate the issue is much clearer. There is a direct dose response relationship between ingestion of perchlorate and the function of the thyroid. What is not clear in the case of both chemicals are the subtle effects of subthreshold doses of the chemicals. For both of these chemicals, will doses below the current California Action Levels result in any long term health effects? Are there sensitive subpopulations (the elderly, the immuno compromised, pregnant women, and children) who will be affected by the presence of residual amounts of the chemicals? Will the costs of treating water for these chemicals prohibit water purveyors from concentrating on other significant treatment issues, e.g., fixing naturally occurring problems (high mineral contents such as arsenic, lead, and mercury), and biological pathogens.

The answers to those questions are not immediately available to consumers or water purveyors. Most toxicological research uses isolated animal or cellular systems to measure response to chemicals. The results are then extrapolated to normal "healthy" populations. Research into sensitive populations is limited by ethical (use of adults or children as subjects in toxicological testing is very limited) and logistical restraints (size of the population and/or mortality rates). The induction period for cancers tend to be very long (on the order of multiple years) and may appear very subtly in a population. Unless the response manifests itself in a unique way, such as a rare cancer, decades will need to pass before any statistically significant relationship will be seen. For endpoints other than cancer, e.g., learning disabilities, infertility, suppressed immune systems, the response in sensitive populations may be difficult to measure given the unusual nature of the population.

What does this mean for water purveyors? Like the case of benzene and Perrier, water purveyors need to take charge of the information disseminated to the public. The standards required by the SDWA and local regulations help ensure the health of the public.

Reintroducing Public Health Into The Risk Management Process - Framing future debates on the social and economic costs of chemicals in the water supplies

As Thomas Burke^{iv} notes the common misinterpretation that the 1983 National Academy of Science "red book" separates the risk assessment process from risk management has led to an "isolation approach to risk characterization and contributed to a departure from traditional public health methods." In his analysis of the public health approach, Burke finds that the public health methods use a bottom up approach. The methods include surveillance of a population to measure a diverse rate of disease/health outcomes in the population. Solutions are devised to improve the community's health through low tech or broad based actions where public values are an essential component of the intervention strategy. Burke notes that the current risk based approach used by regulatory agencies is based on a top down approach focused on a limited health endpoint, normally cancer, and a limited set of hazards, normally pollutant specific. The approaches used to solve the problem are high tech and pollutant specific and do not provide a mechanism for the inclusion of public values.

Like the USEPA's Cardinal Rules of Risk Communication, there are certain rules about risk management that water purveyors need to remember are:

- Communicate (to stakeholders)
- Educate (the public)
- Eliminate (the health concerns)
- Don't hesitate (to take action) or procrastinate
- Don't underestimate (the reaction of the public)
- Try not to litigate (it does not seek the truth!)
- Regulate (to set "safe" or "acceptable" goals)
- Participate (be involved early on and in all steps)

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“A Basin Protection Strategy for Sites with MTBE Impacts”

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INTRODUCTION

The national presence of MTBE at petroleum sites carries the potential to adversely impact groundwater basins and, hence, the municipal and domestic drinking water supply sources producing from them. Municipal water suppliers are required to prepare source water protection plans for their groundwater basins. Unfortunately, these plans may not be specific enough to determine which petroleum sites may pose the greatest risks in the near term. Furthermore, sites with the greatest risk do not often receive proportional attention because the criteria for determining which sites to work on is inconsistent and unclear to all stakeholders. The regulatory debate often focuses on corrective action plans and cleanup criteria for sites that pose no immediate threat to drinking water wells or surface water bodies. Even though no other driver exists (business, political, etc.), the parties responsible for these sites are not allowed to ‘pause’ in order to redirect their efforts to sites posing a more immediate risk. Because resources are limited both from a regulatory and from a business perspective, all sites cannot be investigated and remediated at the same time. Therefore, it is prudent to apply human and financial resources to those posing the greatest threat.

Although risk is often thought of as the primary reason that site work is undertaken, other site drivers commonly override a risk-based decision. Business considerations such as property transfers, pending litigation, or facility construction work may cause a responsible party to undertake work that would not be required based on a purely human health or ecological risk analysis. Although political considerations or adverse press coverage may also drive additional work to be completed at an otherwise low risk site, the predominant driver at many sites has traditionally been regulatory compliance. Unless another driver exists, further work is often deferred until a regulatory directive is received. If a mobile constituent such as MTBE is present under certain subsurface conditions, otherwise manageable plumes may become large enough to impact nearby drinking water wells (or surface water intake) before a regulatory directive is received.

This paper presents a method for regulators, basin managers, or responsible parties with large numbers of sites to determine the likelihood of impacting drinking water wells and the level of action appropriate for each site. The method contains a set of criteria by which sites are ranked based upon the interpreted potential threat to a receptor and the uncertainty associated with the data used to make this interpretation. The site ranking process provides the framework for making resource allocation decisions for a group of sites. The process allows for continual re-ranking of sites as new information becomes available.

PROCESS DESCRIPTION

The site ranking and management process has four steps: I) Compile existing data, II) Rank all sites, III) Select appropriate site subset, and IV) Implement appropriate actions. The process is repeated to generate a new ranking as new information is developed for the sites. Once completed, the highest-ranking sites garner the most immediate attention.

Step I. Compile existing data: Compile existing data and estimate the uncertainty for the following:

- 1) Locations (coordinates) of both source sites and receptor wells,
- 2) Representative groundwater analytical (MTBE) concentrations of the sites, and
- 3) Production rates or number of service connections for the receptor wells.

A database system can be very helpful for evaluating the data associated with large numbers of sites. A Geographic Information System (GIS) can be used to determine the coordinates of wells and sites if addresses or other location information is available. A GIS can also easily calculate the distance between two locations. For these reasons and others, use of a GIS for managing the data for a large number of sites is preferred.

Step II. Rank All Sites: Sites are ranked according to the following criteria:

- 1) Concentration versus distance (C/D) ratio,
- 2) Production rates/number of service connections, and
- 3) Uncertainty level.

The primary criteria of the process involves determining a C/D ratio for each site. The ratio is obtained by dividing the maximum representative MTBE concentration (in ug/l) by the distance (in feet) from the site to the potential receptor. This ratio is used to normalize the risk so that a site with low concentrations located close to a well is treated the same as a high concentration site that is further from a well. The level of current utilization of the drinking water well serves as a secondary criteria so that a relative resource value and potential magnitude of impact is included in the process. The third criteria is the level of uncertainty underlying each data value. Each of these components is further addressed in a subsequent section.

Step III. Select Appropriate Site Subset: Choose the highest-ranking subset of sites for most immediate evaluation. The number of sites chosen will depend on the amount of human and financial resources available. Thresholds must be established to determine the number of sites to be evaluated in more detail during this round of work.

Ideally, sites with the highest C/D ratios nearest to the most utilized wells should be the primary focus. Additionally, sites with a high level of uncertainty and/the potential for near-term impacts, i.e., sites less than 100 feet from a receptor, should be evaluated early in the process. Only sites posing no risk to the receptors are removed from the list. Based on the lower ranking, the remaining sites are put into a 'pause' mode until resources become available to address them. It should be noted that a site which is 'paused' may continue to have monitoring of wells or other low level efforts performed. It is the initiation of further investigation or active remediation which is 'paused'.

Step IV. Implement Appropriate Actions: Determine and implement the appropriate level of action required in order to reduce risk to receptors and/or uncertainty. The level of action appropriate for the higher ranked sites should be commensurate with the level of risk to the receptor. Actions may include well surveys, direct push groundwater sampling, monitoring well installation, risk assessment, source remediation, etc.

UNCERTAINTY

The nature of site assessment guarantees that uncertainty will always exist. However, the level of uncertainty in the data used to rank each site needs to be qualified in order to insure that appropriate decisions are made.

C/D Ratio

Concentration

The concentration portion of the ratio typically represents the maximum concentration historically found at the site if the plume is undefined. Fully defined plumes with historic data may be more accurately represented by the current concentration. The concentration value can be influenced by many factors including type of analysis, sample location/position, sampling interval and sample acquisition timing.

The type of analysis will influence the uncertainty in the measurement. For instance, EPA Method 8020 may give a false positive so it may be prudent to confirm at least one sample per site by EPA Method 8260. Analytical results may vary by up to 40% and still be considered a valid result. Therefore, single samples are usually less reliable than multiple samples with similar results analyzed over time.

The sampling method is important since discrete sample concentrations compared to concentrations from samples representing an average over a well screen length can vary dramatically. Furthermore, sample location (laterally and vertically) must be considered when determining how representative a sample is. Finally, due to the rapid dissolution of MTBE from gasoline (NAPL), the timing of the sample acquisition relative to the release plays a critical role in evaluating the uncertainty of the sample concentration and whether or not it is representative of the site conditions.

If concentration data is not available, it may be necessary to assign a high concentration (ie.effective solubility) and a high uncertainty. If the site is close to a significant receptor, it may be prudent to collect data to reduce the uncertainty to an acceptable level. Other factors must be considered in this decision process such as history of MTBE use, comfort level with the facilities equipment, and future plans for the site.

Distance

Accurate distances between sites and potential receptors are crucial to successfully implementing this process. Any coordinates used for calculating these distances must be evaluated in terms of data quality. For instance, commercially available coordinates have been reported to have errors of up to several hundred feet. When used correctly, Global Positioning System (GPS) receivers may provide the best coordinate data. However, the myriad of GPS receivers vary significantly in the quality of data they are capable of obtaining. Furthermore, GPS operators add another level of variation and therefore all GPS data must also undergo examination. In this regard, it is crucial that all coordinate data be scrutinized and an appropriate uncertainty factor applied.

The function of the migration pathway is another factor that must be included in the distance uncertainty evaluation. In general, releases are shallow and drinking water is extracted from deeper in the aquifer. Therefore, the receptor may be protected by low groundwater flow rates, aquitards and properly installed/completed wells. In contrast, improperly abandoned wells and hydrogeologic parameters that facilitate groundwater movement can increase the risk to a receptor.

Production Well Data

Utilization of water resources requires frequent adjustments to meet demands. Well production can vary on a daily to an annual scale. Also, wells may be abandoned for many reasons. In this regard, it is important that the most current status (and the potential for that status to change) of a potential receptor is known when making ranking determinations. Well construction information is often missing or unreliable and should be carefully reviewed.

Reducing Uncertainty

Gathering additional or more current data generally reduces uncertainty. It is always recommended that the appropriate quality data be collected the first time in order to avoid redundant efforts. A thoroughly developed assessment plan addresses the uncertainties up front.

The first time that the site-ranking list is compiled, the only information that may be available is the site location; both C and D are unknown. In this case, other factors may need to be considered to give it a ranking, such as year that the station was demolished implying a probability that MTBE was ever dispensed from the site. In many cases, it may be appropriate to tolerate higher uncertainties in the short term if the risk is low.

REDUCING RISK

In this basin management process, remediation is performed only at sites with an immediate threat to a receptor or as part of a basin-wide strategy. It may utilize resources more effectively to reduce the uncertainty at all sites to acceptable levels before a basin-wide site remedial strategy is implemented. Migration control may be implemented for near-term protection of a receptor as a plume approaches. In these cases, the options of destroying the well or wellhead treatment must be weighed against long-term migration control. When implemented, pump and treat or other mass reduction strategies are most effective in removing high concentrations from recent releases prior to significant plume migration.

IMPLEMENTATION CONSIDERATIONS

There are many issues to be considered in implementing a plan such as this. For instance, multiple regulatory jurisdictions, staff turnover, cleanup time frame, and level of effort are all issues that must be addressed when implementing this process. However, the process can save time and money by allowing the flexibility to negotiate a round of work on multiple sites rather than on a site by site basis and provides a rational basis for making the necessary decisions. Stakeholders on all sides of the table need to be able evaluate data in the face of uncertainty and determine appropriate actions. To be most effective, stakeholders must form partnerships in the decision making process.

CONCLUSION

The current method for determining which sites should receive human and financial resources often does not reduce immediate risk to drinking water wells. The process outlined in this paper provides a method for stakeholders to better understand which sites pose an immediate risk, a long-term risk, or no risk at all. The method can utilize resources more efficiently and therefore provide better basin-wide protection in a shorter time than traditional decision making processes.

MTBE – THE NEED FOR A BALANCED PERSPECTIVE

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It is very important that we develop a rational and technically defensible approach for dealing with MTBE and other chemicals in groundwater. In order to do this, we all need to work together as stakeholders and address the technical and policy decisions that are critical to the process. While we all have our different perspectives and biases as described below (I'm sorry if I have offended anybody), it is important to use a stakeholder process to find middle ground. This will not be an easy task, especially in dealing with some of the critical policy decisions. So, let's roll up our sleeves and get started!

Most of us think of MTBE as methyl tertiary-butyl ether. This compound has been used in some regions of the country since 1979. Originally, it was used as a blending component (up to 8% v/v) to replace lead as an octane booster. With the advent of the Clean Air Act, it has been used at higher concentrations (up to 15% v/v) to satisfy requirements of the Oxygenated Fuel and Reformulated Gasoline Programs. Although other oxygenates are also used, MTBE is the most widely used oxygenate (U.S. production rates \approx 126,000 b/d) due to both performance and manufacturing factors. Initial data indicates that a significant reduction in carbon monoxide, ozone, benzene, and other air pollutants is occurring due to the use of oxygenated fuels.

Depending on one's perspective, MTBE can mean something more than merely methyl tertiary-butyl ether. The first time that I dealt with an MTBE release was in 1980. After conducting a site assessment, I was amazed to see that MTBE migrated faster and farther than BTEX. Because of this, I quickly developed a different perspective for MTBE (Most Things Biodegrade Easier). With our current level of understanding of basic MTBE properties in relation to BTEX, extended migration (relative to BTEX) is to be expected.

Over the last few years, many of us have become more familiarized with MTBE due to several high visibility problems and the USGS National Water Quality Assessment (NAWQA) well sampling program. During this time, I have observed a variety of perspectives for MTBE. Some environmentalists think of MTBE as a Menace Threatening our Bountiful Environment. On the other hand, I have seen some companies view it as a Major Threat to Better Earnings due to higher site assessment and remediation costs. Because of the potential problem that MTBE poses and with the closure of many UST sites over the last 3 years, some regulators are using MTBE for Movement Towards Bureaucratic Entrenchment. Last but not least, some consultants tend to take advantage of these situations and view MTBE as Money To Be Extracted. These divergent perspectives are making it harder for everyone to deal effectively with the problem. While there may be valid reasons for these different perspectives, we have to ask ourselves how we can balance them to most effectively deal with these groundwater problems in a reasonable manner.

In my opinion, we have the perfect opportunity to further utilize risk-based decision making to promote protection of health, safety, and the environment. This process is being applied very effectively for BTEX compounds and can work for any chemical given that appropriate information is available. In order to achieve this goal, we need to deal with both the technical and policy issues. The three most critical technical issues relating to MTBE from this perspective are:

- 1) **migration of MTBE in the environment** - Through use of existing physical and chemical data (Table 1) and hydrogeologic knowledge, we have enough information to understand MTBE migration from a reasonably conservative standpoint.
- 2) **health and aesthetic (odor, taste) factors** - In December 1997, the U.S. EPA issued a drinking water advisory for MTBE. This advisory allows for a range of 20 to 40 :g/L in drinking water, primarily to avoid adverse aesthetic effects. The EPA further concluded that there is little likelihood that these concentrations would cause adverse health affects since they are 4 to 5 orders of magnitude below the lowest concentration which caused an observable health effect in animals.
- 3) **site characterization** - Determination of adequate requirements will help ensure that the appropriate type and amount of data are obtained within a tiered framework so that risk-based decisions can be made.

With this generic information, or even better, with site-specific information, we can now begin to answer many important questions such as: What concentration of MTBE at a particular point on site will cause an unacceptable concentration at the site boundary or at a downgradient Point of Exposure (POE)? How far will the MTBE plume migrate? How much of a release will cause an unacceptable concentration at the POE? The answers that we obtain will be different than what we would arrive at for benzene because of the significant differences between the two chemicals (Table 1). In answering these questions, we can quickly identify the benefits of release prevention, quick response time, and plume management for MTBE in those areas where groundwater is an actual or reasonably potential drinking water resource.

Due to the relatively wide occurrence and increased migration potential for MTBE as compared to BTEX, it is even more important that key policy issues be reasonably addressed. From my perspective, the two most important issues are **groundwater classification** and **site categorization**. Reasonable groundwater classification in terms of potential drinking water resource is critical. Existing and reasonably potential drinking water aquifers need to be recognized so that facilities that have a potential to impact these zones can be properly managed. On the other hand, classification of groundwater as a potential drinking water supply which has a low probability of ever being used (i.e. low deliverability, poor natural groundwater quality, regional contamination, etc.) will only divert corrective action resources away from sites that truly need help and will likely challenge the viability of State Trust Funds. Finally, a good categorization system (based on urgency of response) will help everyone allocate resources where they are most urgently needed. No matter whether you work for an oil company or a state, there is only so much money in the budget. Even with an unlimited supply of money, we will not have all the other resources (i.e. project managers, consultants, drilling rigs, etc.) we need to address all of the problems at once. A good categorization system will help ensure that the proper level of resources are applied at problematic sites and that we all get "the most bang for the buck".

While we don't have all of the answers yet, we certainly have enough information to get started. The American Petroleum Institute – Soil/Groundwater Technical Task Force has prepared a FAQ sheet which I have included with this article. Other good information can be found on the internet through the EPA, API, USGS, Cal leg./UC Davis, and many other web sites. Finally, by building a technically strong and well-balanced stakeholder group to address MTBE within a risk-based decision making framework, we can achieve the perspective that we should all¹ be striving for "Management Towards a Better Environment".

Table 1
Physical/Chemical Properties

Compound	MW	S (mg/l)	Δ (g/ml)	Pvap (atm)	H (c/c)	Koc	R
Benzene	78	1780	0.88	1E-01	0.22	81	5
Toluene	92	515	0.87	4E-02	0.27	234	11
Ethylbenzene	106	152	0.87	1E-02	0.36	537	25
o-Xylene	106	220	0.88	1E-02	0.23	557	26
m-Xylene	106	160	0.87	1E-02	0.29	612	28
p-Xylene	106	215	0.86	1E-02	0.23	590	27
Naphthalene	128	31	1.15	4E-04	0.02	844	39
Methyl t-butyl Ether	88	42000	0.74	2E+02	0.02	14	1.6
Methanol	32	miscible	0.79	1E+02	0.0001	0.2	1.0
n-Ethanol	46	miscible	0.79	5E+01	0.0012	0.5	1.0

Ref: after TPHCWG Volume #3: $R = \text{retardation} = 1 + \rho_b \cdot f_{oc} \cdot K_{oc} / \eta$ w/ ASTM RBCA Default Parameter Values

¹ MW (molecular weight), S (solubility), Δ (density), Pvap (vapor pressure), H (Henry's Law constant), Koc (organic carbon/water partition coefficient), R (retardation)

POTENTIAL CLAIMS FOR WATER PURVEYORS IMPACTED BY MTBE OR PERCHLORATE – Gregory J. Patterson

I. INTRODUCTION

The threat to groundwater posed by the comparatively recent discovery of methyl tertiary butyl ether ("MtBE") and perchlorate in groundwater places new demands on water purveyors who rely on groundwater as their primary, if not sole, source of potable water. The lack of drinking water standards, the persistence of these chemicals in the environment, and the relatively sparse information regarding the health effects of these chemicals, make it difficult for water purveyors to develop an effective response. In addition to seeking appropriate remedies to remediate the contamination, water purveyors also now find themselves defending against numerous toxic tort claims brought by customers asserting personal injury and property damage claims caused by the delivery of allegedly contaminated water.

In the event litigation becomes necessary, the following reviews potential claims that water purveyors may assert against those parties responsible for contamination. There is also a brief discussion regarding the status of the toxic tort litigation against certain water purveyors currently pending in California.

II. POTENTIAL CLAIMS AGAINST RESPONSIBLE PARTIES

A. *Resource Conservation and Recovery Act (RCRA)*

The Resource Conservation and Recovery Act ("RCRA"), 42 U.S.C. Sections 6901, *et seq.*, provides for civil remedies in the form of injunctive relief and, when applicable, can be a powerful tool to force responsible parties to remediate contamination.

1. *The Citizen Suit Provision*

42 U.S.C. § 6972 states in relevant part:

"[A]ny person may commence a civil action on his own behalf¹ ... (b) against any person, including the United States and any other governmental instrumentality or agency, to the extent permitted by the eleventh amendment to the Constitution, and including any past or present generator, past or present transporter, or past or present owner or operator of a treatment, storage, or disposal facility, who has contributed or who is contributing to the past or present handling, storage, treatment, transportation, or disposal of any solid or hazardous waste which may present an imminent and substantial endangerment to health or the environment ..."

42 U.S.C. § 6972(a)(i)(B).

RCRA provides for injunctive relief only. Recovery of past clean-up costs is not an available remedy. See Meghriq v. KFC Western, Inc., 516 U.S. 479, 116 S.Ct. 1251 (1996).

The following addresses several key elements of a RCRA claim.

¹ RCRA defines "person" as "... an individual, trust, firm, joint stock company, corporation (including a government corporation), partnership, association, state, municipality, commission, political subdivision of a state, or any interstate body and shall include each department, agency, and instrumentality of the United States."

a. *Definition Of Solid Waste*

RCRA's statutory definition of "solid waste" is broadly defined as:

[A]ny garbage, refuse, sludge from a waste treatment plant, water supply, treatment plant, or air pollution control facility and other discarded material, including solid, liquid, semi solid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations..."

42 U.S.C. § 6903(27)

Courts have had little difficulty determining that gasoline leaking from underground storage tanks is a solid waste under RCRA. See, e.g., Zands v. Nelson, 779 F.Supp. 1254, 1262 (S.D. Cal. 1991); Craig Lyle Limited Partnership v. Land O'Lakes, 877 F.Supp. 476, 480-482 (D.Minn. 1995); Paper Recycling v. Amoco Oil Company, 856 F.Supp. 674-676 (N.D. Ga. 1993).

b. *Definition Of Imminent And Substantial Endangerment*

To prevail in a § 6972(a)(1)(B) claim, a plaintiff must show that the solid or hazardous waste "may present an imminent and substantial endangerment to health or the environment."

Courts construing the imminent and substantial endangerment provision have held that "imminency" does not require a showing that actual harm will occur immediately so long as the risk of threatened harm is present. An imminent hazard may be declared at any point in the chain of events which may ultimately result in harm to the public. Environmental Defense Fund, Inc. v. Environmental Protection Agency, 465 F.2d 528, 535 (D.C. Cir. 1972). Courts have consistently held that endangerment means threatened or potential harm and does not require proof of actual harm. United States v. Ottati & Goss, Inc., 630 F.Supp. 1361, 1394 (D.N.H. 1985); United States v. Vertac Chemical Corp., 489 F.Supp. 870, 885 (E.D. Ark. 1980); Zands v. Nelson, 797 F.Supp. 805, 809 (S.D. Cal. 1992); Dague v. Burlington, 935 F.2d 1343 (2d Cir. 1991) (reversed on other grounds, 112 S. Ct. 2638 (1992)).

c. *Notice Requirement*

No action may be commenced prior to ninety days after the plaintiff has given notice of the endangerment to: (1) the Administrator of EPA; (2) the state in which the alleged endangerment may occur; (3) any person alleged to have contributed or to be contributing to the past or present handling, storage, treatment, transportation, or disposal of any solid or hazardous waste. 42 U.S.C. § 6972(b)(2)(A).

d. *Recovery Of Costs And Attorneys' Fees*

Attorney fees may be recoverable under RCRA. 42 U.S.C. § 6972(e) allows the court to award costs of litigation, including reasonable attorney and expert witness fees, to the prevailing or substantially prevailing party "whenever the court determines such an award is appropriate."

e. *Shifting Of Burden Of Proof To Defendants To Prove They Did Not Cause The Contamination*

Under certain circumstances a plaintiff may shift the burden to the defendants to prove they did not cause the contamination. Zands v. Nelson, 797 F.Supp. 803 (S.D. Cal. 1992). In Zands, the owners of property upon which a gas station had operated brought an action under RCRA against prior owners and operators of the gasoline station. Recognizing that plaintiffs could not prove exactly when the contamination occurred, other than it occurred generally during the defendants' operations, the court fashioned the following rule shifting the burden to the defendants to prove that the contamination did not occur during their operation of the station: (1) where plaintiff identifies a period a time during which a contamination occurred; (2) owners of the property or operators of the gas station are strictly liable for the contamination of the property that occurred during their period of ownership or operation; (3) where plaintiff joins as defendants all persons who owned the property or operated the gas station for at least a portion of the time during which the contamination occurred; (4) but where plaintiff cannot prove which owner or operator caused the contamination because more than one person owned the property and operated the gas station during the period of known contamination; (5) then the court will shift the burden to each of the owner/operator defendants to show that the contamination did not occur during the period of the defendants' ownership or operation.

f. *Action Barred By Federal/State Action*

Under RCRA, no party may bring a citizen suit if the Administrator or the state has commenced and is diligently prosecuting an action; is engaged in a removal action; or is incurring costs to initiate a remedial investigation and feasibility study. 42 U.S.C. § 6972(b)(2)(A), (B) and (C). The courts have interpreted this section to mean that an administrative action does not constitute an "action" under the statute and does not bar a private citizen suit under RCRA. Rather, the federal or state agency must assert a court action to bar a citizen suit. See, e.g., Coalition for Health Concern v. LWD, Inc., 834 F. Supp. 953, 955-956 (W.D. Ky. 1993) (reversed on other grounds 60 F.3d 1188); Lykins v. Westinghouse Electric Corporation, 715 F. Supp. 1357 (1989).

g. *Burfurd Abstention*

Even in circumstances where there is only a state or federal administrative action, a federal court has discretion to decline to exercise jurisdiction of a RCRA claim under the Burfurd Abstention Doctrine in those instances:

"... when there are difficult questions of state law bearing on policy problems of substantial public import whose importance transcends the result in the case then at bar; or (2) where the exercise of federal review of the question in a case and in similar cases would be disruptive of state efforts to establish a coherent policy with respect to a matter of substantial public concern."

Coalition for Health Concern v. LWD, Inc., 60 F.3d 1188, 1194 (6th Cir. 1995).

B. *Comprehensive Environmental Response Compensation And Liability Act ("CERCLA"), 42 U.S.C. § 9601, et seq.*

1. *Elements Of CERCLA Claim*

42 U.S.C. § 9607(a) allows recovery by a party of any "necessary costs of response (to a release of a hazardous substance) ... consistent with the national contingency plan." 42 U.S.C. § 9607(a)(4)(B).

The claim may be asserted against (1) the owner and operator of a vessel or facility; (2) any person who at the time of disposal of any hazardous substance owned or operated any facility at which such hazardous substances were disposed of; (3) any person who by contract, agreement, or otherwise arranged for disposal, treatment or transportation of a hazardous substance; and (4) any person who accepts or accepted any hazardous substance for transport to disposal or treatment facilities. 42 U.S.C. § 9607(a) (1-4). Liability under CERCLA is strict and several.²

2. *The Petroleum Exclusion*

With respect to MtBE contamination, a critical threshold question is whether MtBE falls under the petroleum exclusion.

Under CERCLA, the term hazardous substance "does not include petroleum, including crude oil or any fraction thereof which is not otherwise specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of this paragraph." 42 U.S.C. § 9601(14).

EPA has issued an Opinion of the General Counsel on the scope of the petroleum exclusion under CERCLA. It is EPA's position that contaminants present in used oil or any other petroleum substance are not within the petroleum exclusion. "Contaminants" are defined as substances not normally found in refined petroleum fractions or present at levels which exceed those normally found in such fractions. If the contaminants are CERCLA hazardous substances, they are subject to CERCLA response authority and liability. (EPA Memoranda dated July 31, 1987.)

EPA's interpretation of "petroleum" under CERCLA § 101(14), however, also includes hazardous substances which are normally mixed with or added to crude oil or crude oil fractions during the refining process. EPA notes "these substances are also part of 'petroleum' since their addition is part of the normal oil separation and processing operations in the refinery in order to produce the product commonly understood to be petroleum."

The Ninth Circuit has interpreted the petroleum exclusion in a manner similar to that of EPA in Wilshire Westwood Assocs. v. Atlantic Richfield Corp., 881 F.2d 801 (9th Cir. 1989). In Wilshire Westwood, plaintiff sued Atlantic Richfield to recover costs arising from the contamination caused by leaking underground storage tanks. The contamination consisted primarily of gasoline, including leaded gasoline. Plaintiffs argued that lead and certain additives such as benzene and toluene were not covered by the petroleum exclusion. The Ninth Circuit disagreed. Essentially following the EPA opinion, the Ninth Circuit ruled that the petroleum exclusion applies to unrefined and refined gasoline even though certain of its indigenous components and certain additives placed in the gasoline during the refining process have themselves been designated as hazardous substances within the meaning of CERCLA. Id. at 810.

In part, the Ninth Circuit noted that the construction advocated by plaintiffs would have the effect of rendering the petroleum exclusion a nullity because crude oil petroleum and petroleum fractions -- unrefined or refined -- would fall outside the exclusion due to the inclusion of substances considered hazardous under CERCLA. The Central District has ruled in a similar fashion in Southern Pacific Transportation Company v. California, 790 F.Supp. 983 (C.D. Cal. 1991). In Southern Pacific the court ruled that the petroleum exclusion applies even though CERCLA listed hazardous substances are indigenous in the petroleum or are additives normally added to the petroleum during the refining process. Id. at 984 (emphasis added). The Southern Pacific court also ruled that soil contaminated with petroleum also falls under the petroleum exclusion noting that the "sheltering sweep of the petroleum exclusion is not affected by the presence or absence of soil." Id. at 986.

² Generally, a Section 107(a) action cannot be brought by a party designated as responsible under Section (a)(1-4). Those parties are limited to a contribution action under Section 113 (42 U.S.C. § 9613).

Unlike toluene and benzene, MtBE is not "crude oil" or "any fraction thereof" and is added to gasoline after the refining process. However, allowing CERCLA claims for gasoline contamination containing MtBE would essentially render the petroleum exclusion meaningless. Asserting this claim likely will result in vigorous litigation regarding the scope of the petroleum exclusion.

C. *State Superfund Laws*

Most states have enacted legislation similar to CERCLA. For instance, in California, Health & Safety Code § 25363(e) provides: "[a]ny person who has incurred removal or remedial action costs in accordance with this chapter or the federal act may seek to recover these costs from any person who is liable pursuant to this chapter . . ." Again, however, the claim may be precluded by the petroleum exclusion found at Health & Safety Code § 25317 which has been interpreted as broadly as the federal petroleum exclusion under CERCLA.

D. *Claim Under California Constitution, Article 10, Section 2*

California Constitution, Article 10, Section 2, provides in relevant part:

"It is hereby declared that because of the conditions prevailing in this state, the general welfare requires that the water resources of the state be put to beneficial use to the fullest extent of which they are capable, and that the waste or unreasonable use or unreasonable method of use of water be prevented, and that the conservation of such waters is to be exercised with a view to the reasonable and beneficial use thereof in the interest of the people and for the public welfare."

A private right of action exists under this section based on a theory that the contamination of groundwater sources constitute "waste" and "unreasonable use or unreasonable method of use of water".

E. *Continuing Nuisance*

Nuisance is statutorily defined in California:

"Anything which is injurious to health, or is indecent or offensive to the senses, or an obstruction to the free use of property, so as to interfere with the comfortable enjoyment of life or property, or unlawfully obstructs the free passage or use, in the customary manner, of any navigable lake, or river, bay, stream, canal, or basin, or any public park, square, street, or highway, is a nuisance."

Civil Code § 3479

There is substantial case law holding that the contamination of property constitutes a nuisance. See e.g., Mangini v. Aerojet-General Corp., 230 Cal.App. 3d 1125, 281 Cal.Rptr. 827 (1991); Capogeannis v. Superior Court, 12 Cal.App. 4th, 668, 15 Cal.Rptr. 2d 796 (1993); Newland Farming Company v. Superior Court, 19 Cal.App. 4th, 334 23 Cal. Rptr. 2d 377 (1993); Camsi IV v. Hunter Technology Corp., 230 Cal.App. 3d 1525, 282 Cal.Rptr. 80 (1991); Wilshire Westwood Associates v. Atlantic Richfield Co., 20 Cal.App. 4th, 732, 24 Cal. Rptr. 2d 562 (1993); KFC Western, Inc. v. Meghriq, 23 Cal.App. 4th, 1167, 28 Cal. Rptr. 676 (1994).³ To recover under a continuing nuisance theory, a plaintiff must show that the contaminated condition is *abatable*, i.e., subject to remediation or clean up, and that the cost of clean up is reasonable. Mangini v. Aerojet Gen'l Corp., 12 Cal.4th 1087, 1103, 51 Cal.Rptr.2d 272 (1996). "[T]he crucial test of the permanency of a trespass or

³ The common law claims are based on California law. Common law theories may differ in other states.

nuisance is whether the trespass or nuisance can be discontinued or abated.” *Id.* at 1097 (quoting *Mangini I*, 230 Cal.App.3d 1125, 1148 (1991)).

F. Continuing Public Nuisance

A public nuisance is one which affects at the same time an entire community or neighborhood, or any considerable number of persons, although the extent of the annoyance or damage inflicted upon individuals may be unequal. Civil Code § 3480.

Remedies for both public and private nuisances include abatement through injunction and damages caused by the nuisance. Civil Code § 3484; Civil Code § 3491.

G. Continuing Trespass

Trespass is an unlawful interference with possession of property. *Mangini v. Aerojet-General Corp.*, 230 Cal.App. 3d 1125, 1141 (1991).

Plaintiffs, when asserting a trespass claim, generally rely on Section 160 of the Restatement Second of Torts which provides in pertinent part:

"A trespass may be committed by the continued presence on the land of a structure, chattel, or other thing which the actor or his predecessor in legal interest has placed on the land."

Mangini at 1141, 1142.

Additionally, under the Restatement Second of Torts, § 161(1) a "trespass may be committed by the continued presence on the land of a structure, chattel, or other thing which the actor has tortiously placed there, whether or not the actor has the ability to remove it." Tortious conduct denotes that conduct, whether of act or omission, which subjects the actor to liability under the principles of the law of torts. *KFC Western, Inc. v. Meghriq*, 23 Cal.App. 4th 1167, 1181 (1994).

In order to be actionable, the trespass must be tortious, that is either intentional or negligent. A private nuisance is a "civil wrong" and one who causes a public nuisance likewise is considered a tortfeasor because a creation of either a private or public nuisance is tortious and such conduct may support a claim for trespass. *KFC Western*, at 1181, 1182.

H. Safe Drinking Water And Toxic Enforcement Act Of 1986

1. Proposition 65

Health & Safety Code § 25249.5 provides in relevant part:

"No person in the course of doing business shall knowingly discharge or release a chemical known to the state to cause cancer or reproductive toxicity into water or into land where such chemical passes or probably will pass into any source of drinking water."

MtBE and perchlorate are not chemicals currently listed under Proposition 65 as chemicals known to the state to cause cancer or reproductive harm. However, with respect to MtBE contamination caused by a release of gasoline, other gasoline constituents, such as benzene and toluene are. Further, perchlorate is often found with other listed chemicals such as perchloroethylene.

A discharge is exempt if it will not result in any "significant amount" of a listed chemical entering any source of drinking water, and the discharge is in compliance with all applicable regulations, permits and orders. Health & Safety Code § 25249.9. A "significant amount" is defined as "any detectable amount" unless the defendant can show that the exposure to the discharged chemical and drinking water presents "no significant risk" of cancer, assuming lifetime exposure at the level of discharge, or that the exposure will have no observable reproductive effect, assuming exposure at 1,000 times the level of discharge. Health & Safety Code §§ 25249.10, 25249.11.

The regulations define a discharge or release to include the depositing of listed chemicals in either surface or groundwater or onto or into land which "more likely than not will pass into a source of drinking water." 22 C.C.R. § 12401(e)(1)(3).

Under subdivision (d), an action may be brought by any person in a public interest if (1) the action is commenced more than sixty days after the period has given notice of the violation which is the subject of the action to the Attorney General, and the District Attorney, and any City Attorney in whose jurisdiction the violation has alleged to occurred and to the alleged violator, and (2) neither the Attorney General nor a District Attorney nor a City Attorney or a prosecutor has commenced and is diligently prosecuting an action against such violation. Health & Safety Code § 25249.7.

Remedies under Proposition 65 include injunctive relief enjoining the conduct and civil penalties of up to \$2,500 per day for each such violation. Health & Safety Code § 25249.7. Attorneys fees also are recoverable.

The claims described above are not meant to be an exhaustive review of all claims which might be asserted by a water purveyor who finds its water source contaminated. Statutory and common law remedies vary state to state. Water purveyors seeking restoration of contaminated water sources should carefully review their litigation options prior to filing suit.

III. RECENT TOXIC TORT LITIGATION AGAINST WATER PURVEYORS

Recently, a number of toxic tort claims, involving in some instances hundreds of plaintiffs, have been asserted against water purveyors. Plaintiffs in these lawsuits allege that they have suffered personal injury and property damage caused by the delivery of contaminated water. Perchlorate is one of the chemicals specifically identified in many of these lawsuits. Plaintiffs' claims raise serious and far reaching implications for water purveyors and the manner in which California and other states manage and regulate their water resources.

A. Summary of Plaintiffs' Claims

Plaintiffs in the toxic tort litigation have asserted claims against the water purveyors for negligence, negligence per se, wrongful death, strict liability, trespass, public and private nuisance, ultra-hazardous activity and fraud. While the lawsuits vary somewhat in content, the complaints generally assert that the water purveyors used, distributed, sold and supplied contaminated water to plaintiffs while knowing that persons such as plaintiffs would risk exposure to the chemicals thereby creating a substantial risk of harm to plaintiffs. Plaintiffs assert that in delivering contaminated water, the water purveyors breached their duty to their customers to deliver safe water and failed to warn plaintiffs of the contamination. In most instances, plaintiffs seek general damages, costs of medical and hospital expenses, both past, present and future, loss of earnings and diminished earning capacity, property damages and injunctive relief preventing the distribution of contaminated water for public consumption. Plaintiffs also seek punitive damages from each of the water purveyor defendants.

B. Recent Action By The Public Utilities Commission

In California, many water purveyors are regulated by the Public Utilities Commission ("PUC"). In response to the lawsuits, the PUC issued an Order Instituting Investigation ("OII") on March 12, 1998. The express purpose of the OII is to examine whether the PUC's drinking water standards and policy adequately protect the public health and safety, and whether water utilities regulated by the PUC are complying with those standards and policies.

As of the writing of this paper, a number of water utilities have filed motions with the California Superior Courts asserting that these courts lack jurisdiction to adjudicate the lawsuit because of the PUC's exclusive jurisdiction. The utilities argue that state wide drinking water policy should be determined by the PUC and not by various state courts whose decisions and findings may conflict with the PUC. This issue should be resolved by the courts in at least two state actions by the date of this conference and likely will be the subject of appeal.

The Analysis for Perchlorate by Ion Chromatography: The California DHS Method

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Abstract

An ion chromatography (IC) method for the determination of perchlorate at low ppb ($\mu\text{g/L}$) levels in groundwater is described. A commercially available anion exchange column and an eluent consisting of 120 mM sodium hydroxide and 2 mM p-cyanophenol (as a modifier) were found to effectively separate the perchlorate anion from other anions commonly found in groundwaters. To enhance analyte detection and measurement, the conductivity of the eluent was chemically suppressed with an inline suppressor device. Following column separation and chemical suppression, the perchlorate anion was detected and measured with a conductivity detector. By employing a large volume sample loop (740 μL), a method detection limit of 1 ppb in reagent water and a linear working range of 4 to 100 ppb were achieved. Using readily available technology, this method may be easily applied by water utility and commercial analytical laboratories familiar with the protocols in USEPA Method 300.0 (Revision 2.1, August 1993) for ion chromatography. Used properly, this method is also capable of meeting the performance standards described in the quality control section of Method 300.0.

Microbiological treatment of perchlorate contaminated ground waters

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Abstract

There are numerous strains of microorganisms capable of reducing both chlorate and perchlorate under anoxic conditions. These strains can easily be cultivated within biofilm reactors for water and wastewater treatment. Mixed cultures were developed in 14.2-cm long sand columns fed an artificial groundwater amended with acetate, trace minerals and nutrients (ammonia and phosphorus) and contaminated with 20 mg/L of perchlorate. Oxygen was removed within the column by the microbial consortia producing anoxic conditions. Perchlorate was removed to below detectable levels ($<4 \mu\text{g/L}$) at loading rates of 0.11 gpm/ft^2 ; at 0.12 gpm/ft^2 , effluent concentrations were $154 \mu\text{g/L}$ and increased rapidly with hydraulic loading. These results indicate that it should be possible to treat perchlorate contaminated drinking water either in sand columns during water treatment, or through subsurface bioremediation.

Introduction

Recent improvements in the detection of perchlorate (ClO_4^-) has indicated that it become a widespread contaminant of water. Samples taken from the Las Vegas Wash, which feeds Lake Mead and then the Colorado River, contained 1,500 to 1,680 ppb, while 8 ppb have been found in water in Lake Mead; the Southern Nevada Water Authority has found 11 ppb of perchlorate in its tap water. Perchlorate has contaminated numerous ground waters in California (30% of 232 wells sampled) at concentrations ranging from $5 \mu\text{g/L}$ (detection limit) to 0.37%. The California Department of Health Services (CDHS), based on EPA work, has established a provisional action level for perchlorate of 18 ppb for drinking water due to perchlorate's interference with iodine in the production of hormones in the thyroid (Urbansky, 1997).

It has been known for over 40 years that chlorate can easily be removed under anoxic conditions by mixed culture. Bryan and co-workers proposed using chlorate respiring microorganisms (CRMs) in a test to evaluate the concentration of biodegradable organic matter in domestic wastewater by measuring the amount of Cl^- produced from the reduction of ClO_3^- (Bryan and Rohlich, 1954; Bryan, 1966). These tests demonstrated not only that chlorate could be reduced by microorganisms, but that chlorate was non-toxic to wastewater bacterial assemblages at concentrations $<1,000 \text{ mg/L}$. While perchlorate is difficult to remove abiotically from water, several microbial strains have been isolated that can degrade both chlorate and perchlorate. Strains known to degrade the indicated halo-oxygenated compounds include: chlorate and perchlorate, *Vibrio dechloraticans* Cuznesove B-1168 (Korenkov et al., 1976); chlorate, *Ideonella dechloratans* (Malmqvist et al., 1994); perchlorate, *Wolinella succinogenes* (Wallace et al., 1996); bromate, *Pseudomonas fluorescens* (Hijnen et al., 1995); chlorate, by isolate GR1, a strain identified to belong to the β subgroup of *Proteobacteria* (Rikken et al. 1996); and chlorate, by isolate AB1, identified as most similar to *Comomonas testasteroni* using a Biolog test (Bliven 1996).

There is little published data on the growth kinetics of perchlorate-respiring microorganisms (PRMs). However, the biochemical similarity of strains capable of respiring both chlorate and perchlorate suggests that data obtained for perchlorate cultures is applicable to chlorate cultures. In order to design a biological treatment process, for example in order to calculate a reactor detention time or loading rate (Logan et al. 1998), uptake and growth data must be known. In order to determine growth rate constants for mixed

cultures under chlorate-reducing conditions, chemostat experiments were conducted using nitrogen-air purged reactors fed different substrates: acetate, glucose-glutamic acid, and phenol. It was found that maximum growth rates using acetate, glucose-glutamic acid, and phenol were 0.56, 0.12 and 0.040 h^{-1} , with cell yields of 0.12, 0.41, and 0.12 g-cell/g-substrate, respectively (Logan et al. 1998). These results indicate that growth rates of CRMs are quite high, and indicate that it should be possible to design water treatment systems using these mixed microbial cultures. To demonstrate that, we report here preliminary data on perchlorate biodegradation in biofilm-containing sand columns.

Methods

Glass columns (Chromaflex; 2.54 cm diameter, 14.2 cm long) were packed with a sandy soil from Tucson, Arizona. This soil was collected 3 to 6 feet below the surface from the North Fallow Field at the University of Arizona farm. The soil has an average particle diameter of 127 μm , a uniformity coefficient of 2.45, and is composed of 90% sand, 7% silt, 3% clay, and has an organic carbon content of 0.07%. Columns were packed dry using a tap and fill procedure, and had all Teflon fittings and 500 μm pore size mesh at the column entry and exit. Water was fed into the column using a positive displacement pump at rates between 1.18 to 3.05 ml/min. All tubing was made of silicon.

A mixed microbial consortium capable of degrading perchlorate was developed by adding perchlorate (1 g/L) to a 1% wastewater sample obtained from the primary digester at the State College Wastewater Treatment Plant. This suspension was incubated in several crimp-top serum bottles (120 ml, with headspace purged with N_2 gas) at room temperatures for 7 days, then transferred (10%) into water containing 1 g/L of acetate and 1 g/L of perchlorate. The ability of this consortium to degrade perchlorate was evidenced by 39% removal perchlorate within 4 days. The column reactors were then inoculated with this acclimated consortium, and left for 1-day prior to pumping. Columns were then operated for several days to develop a biofilm containing perchlorate degrading microorganisms.

An artificial groundwater (AGW) based on the composition of granitic rock aquifer (Graham et al. 1996) was used in column studies. The water consisted per liter of deionized water, of: 6.5 mg of MgSO_4 , 4.3 mg $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 5.85 mg of NaCl , and 48.0 mg of CaCO_3 . To this AGW, we added in column biodegradation studies: 100 mg/L acetate, 20 mg/L perchlorate, and nitrogen and phosphorus at a ratio of 100:23:4.3 as C: N: P. All samples were immediately filtered through 0.2 mm polycarbonate filters (Poretics Corp.) to remove bacteria prior to chemical analysis.

Perchlorate and acetate were measured using a Dionex 100 ion chromatograph equipped with an autosampler and an AS-11 (Dionex) column. Perchlorate was analyzed using a procedure recently developed by Dionex (Dionex application note 121). Briefly, perchlorate was analyzed using a 100 mM NaOH eluent. External water mode was required using a suppressor (ASRS-I). Sample loops of 25 μL and 1000 μL were used to measure concentrations of perchlorate down to a detection limit of 4 $\mu\text{g/L}$. Acetate was measured using the same setup, but with a 0.5 mM NaHCO_3 and 1.5 mM Na_2CO_3 . For each set of measurements, a three point calibration curve was used.

Results and Discussion

At hydraulic loadings of 0.06 to 0.11 gpm/ft^2 , perchlorate was removed to below the California drinking water standard of 18 $\mu\text{g/L}$, and to below detectable levels ($<4 \mu\text{g/L}$) except at 0.09 gpm/ft^2 where the

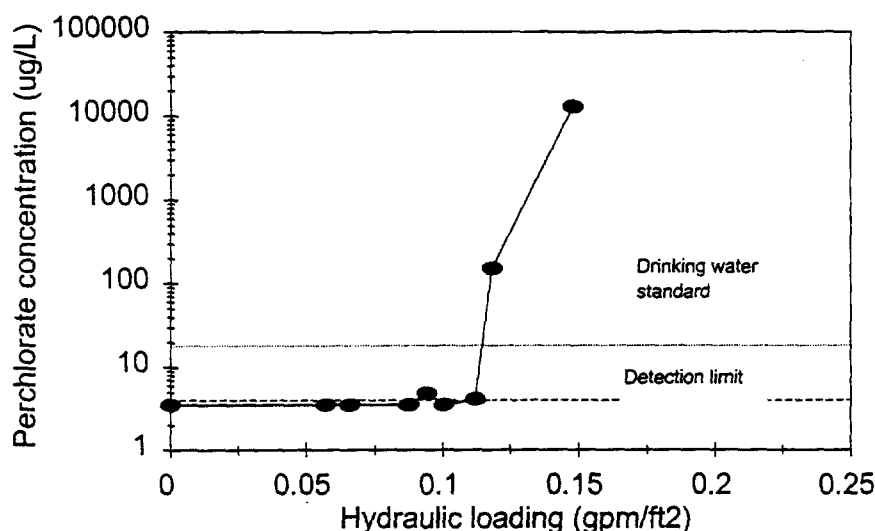


Figure 1. Perchlorate concentrations in column effluent as a function of hydraulic loading rate. Columns were fed an artificial groundwater amended with acetate, nutrients, and 20 mg/L of perchlorate.

perchlorate concentration of 4.8 $\mu\text{g/L}$ was just above our detection limit (Figure 1). These removals translate to >99.98% based on the influent concentration of 20 mg/L of perchlorate. At the two higher loadings tested, we observed breakthrough in the column at 152 $\mu\text{g/L}$ at 0.12 gpm/ft². When the loading was 0.15 gpm/ft², we observed a breakthrough concentration of 12.7 mg/L. Acetate was fed to this reactor at high concentrations (100 mg/L), and acetate remained in excess concentration in the reactor effluent. Acetate concentrations at steady state operation at hydraulic loadings of 0.085 and 0.11 gpm/ft² were 59 and 84 mg/L, respectively.

These preliminary experiments demonstrate that it is possible to remove perchlorate from water by developing a perchlorate-respiring consortium of microorganisms as a biofilm on sand in a packed bed reactor. Although low loading rates (<0.11 gpm/ft²) were necessary here to remove perchlorate to drinking water standards, the bed length used in our experiments was only 14.2 cm long. However, conventional drinking water sand filters, which operate at higher hydraulic loading rates (in the range of 2-5 gpm/ft²), may be suitable for treatment because of their longer lengths. Scaling our results based only on a detention time of ~10 minutes, would require a typical water treatment filter loaded at 0.6 gpm/ft² for a filter 6-ft in length. In general, growth rates and cell yields of chlorate respiring microorganisms examined in our laboratory are among the highest known for anaerobes (Malmqvist et al. 1991; Logan et al. 1998), making it likely that perchlorate-respiring strains could compete well in a biofilm community.

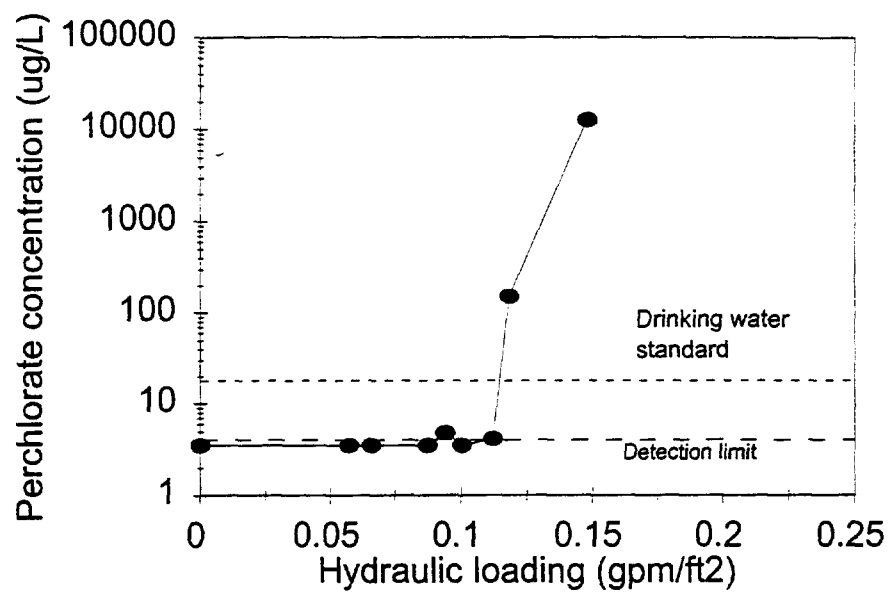
If perchlorate reduction can be so easily driven in laboratory sand columns, then it is likely that *in-situ* bioremediation could also be accomplished. Limiting factors for intrinsic remediation are likely: an absence of sufficient quantities of oxidizable substrate, or, competition for these substrates by other microorganisms; limiting nutrients such as nitrogen and phosphorus. Thus, addition of these compounds to contaminated soils should promote *in-situ* remediation. Early tests on samples from the Nevada Wash area indicate the presence of chlorate and perchlorate respiring microorganisms. However, we need to conduct additional tests to determine their abundance and ecological roles at perchlorate contaminated sites.

Acknowledgments

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MICROBIAL CONVERSION OF PERCHLORATE, CHLORATE AND CHLORITE

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Abstract

Recently, several microorganisms have been described that can obtain energy for growth by coupling the oxidation of organic or inorganic material to the dissimilatory reduction of (per)chlorate to chloride. Evidence has been gathered that the two-step reduction of perchlorate to chlorite is catalyzed by a single (per)chlorate reductase. Chlorite, in turn, is disproportionated into chloride and oxygen. This reaction is catalyzed by chlorite dismutase, a heme iron enzyme. The oxygen generated is also reduced by the microorganisms to maintain anaerobic conditions.

An enrichment culture was obtained from activated sludge that was able to oxidize hydrogen gas with chlorate as electron acceptor in a gas-lift reactor with pumice particles as carrier. A chlorate removal of >95% was observed at hydraulic retention times (HRTs) up to 6 hours. The release of chloride was proportional to the disappearance of 0.5 g/L chlorate present in the wastewater. Reduction of (per)chlorate and dismutation of chlorite at 2.0 mg/L was studied in a packed bed reactor to treat potable water. HRTs of 0.2, 8 and 120 minutes were sufficient for almost complete removal of chlorite, chlorate and perchlorate, respectively

Introduction

Perchlorate, chlorate, chlorine dioxide and hypochlorite are produced on a large scale and used in a wide range of applications. In water chlorine dioxide and hypochlorite decompose into chlorite, chlorate and chloride. Chlorite, in turn, is converted slowly into chlorate and chloride. As a result of the wide variety of applications chloro-oxo acids are present in wastewater, groundwater and drinking water. During the last few years efforts have therefore been made to remove chloro-oxo acids from water by either physicochemical or biotechnological methods (Korenkov *et al.* 1976; Malmqvist *et al.* 1991; Ataway and Smith 1991; Gonce and Voudrias 1994).

Interest in biotechnological water treatment has resulted in the isolation of bacteria which convert perchlorate and chlorate into chloride (Stepanyuk *et al.* 1992; Malmqvist *et al.* 1994, van Ginkel *et al.* 1996; Wallace *et al.* 1996). These bacteria can utilize perchlorate and chlorate instead of oxygen as a terminal electron acceptor. In this paper we describe the physiology of (per)chlorate-utilizing bacteria and the enzymes involved. In addition, applications of immobilized (per)chlorate-reducing microorganisms in a gas-lift reactor and in a packed bed to remove chloro-oxo acids from wastewater and drinking water, respectively, are presented.

Physiology of (per)chlorate utilizing bacteria

(Per)chlorate reducing bacteria are basically aerobic microorganisms that have the alternative capacity to reduce perchlorate and chlorate when oxygen becomes limiting. This capacity is spread among a variety of bacteria. The energy sources of (per)chlorate-reducing microorganisms include organic and inorganic compounds (van Ginkel *et al.* 1995). An isolate designated as GR-1 grew with acetate as carbon and energy source and (per)chlorate, oxygen, or nitrate as electron acceptor. Physiological studies demonstrated that the first steps in the reduction process (perchlorate to chlorite) are accompanied by the oxidation of acetate. The first steps are therefore coupled to energy production. The free energy changes of oxidation reactions coupled to (per)chlorate reduction are high in comparison to oxygen (Milazzo and Caroli 1978). Thus, the largest amount of energy can be gained by utilization of perchlorate. It is therefore surprising that oxygen is the preferred electron acceptor and that the molar growth yields with oxygen, chlorate and perchlorate are comparable (Malmqvist *et al.* 1991). This only makes sense when chlorite reduction is not coupled to energy production because the standard free energy changes of the acetate

oxidation with perchlorate to chlorite and with oxygen are -801 and -844 kJ (mol acetate)⁻¹, respectively (Rikken *et al.* 1996). Indeed, GR-1 catalyzes the dismutation of chlorite into chloride and molecular oxygen which does not yield energy for biosynthesis. The oxygen generated is reduced simultaneously by GR-1 to enable (per)chlorate reduction under anaerobic conditions. The pathway of perchlorate reduction is depicted in Figure 1 (Rikken *et al.* 1996).

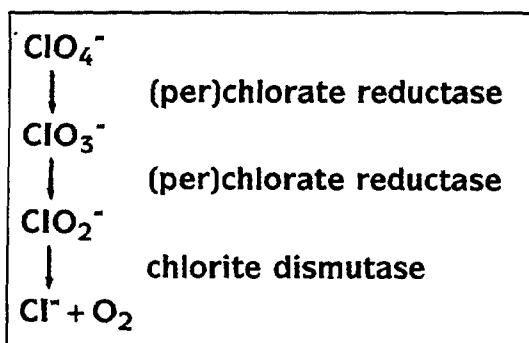


Figure 1
Proposed reduction pathway for perchlorate

Properties of enzymes involved in reduction of perchlorate to chloride

(Per)chlorate reductase

The enzymology of perchlorate reduction was recently investigated. A perchlorate reductase was purified from a culture of strain GR-1 grown on perchlorate. This enzyme is membrane associated. The molecular weight was estimated by gel filtration to be about 420 kDa and by SDS electrophoresis, proteins with apparent molecular weights of 100 and 40 kDa were detected. Solutions of purified reductase were yellow, and the spectrum obtained for the pure protein is consistent with that of an iron-sulfur protein. It was established that molybdenum is associated with the enzyme.

The perchlorate reductase reduced chlorate and nitrate in addition to perchlorate. Apparently, a single enzyme therefore catalyzes both perchlorate and chlorate reduction in GR-1. Methylviologen was used as artificial electron donor for both perchlorate and chlorate reduction. The perchlorate reductase purified showed V_{\max} values of 7.3 $\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$ protein for perchlorate and 13.2 $\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$ protein for chlorate. The K_m for perchlorate is far higher than the K_m for chlorate (Table I). The product of the two-step reduction of perchlorate is chlorite (Figure 1).

Chlorite dismutase

Chlorite is not liberated from (per)chlorate-reducing cells of strain GR-1. Effective conversion of chlorite into chloride and oxygen was therefore attributed to a distinctive enzyme (Rikken *et al.* 1996). The molecular weight of this enzyme estimated by gel filtration is 140 kDa. The enzyme contained four identical 32 kDa subunits. Per subunit, it contains 0.9 molecule of protoheme IX and 0.7 molecule of iron. Only chlorite is a substrate for the enzyme, the K_m and V_{\max} being 170 μM and 2,200 $\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$ protein, respectively (Table I). The products of chlorite conversion by this novel type of heme iron enzyme are always oxygen and chloride (Figure 1). The characteristics of chlorite dismutase clearly distinguish it from other heme enzymes such as catalases and peroxidases (van Ginkel *et al.*, 1996).

Table I Kinetic parameters of (per)chlorate reductase and chlorite dismutase.

Enzyme	Substrate	V_{\max} ($\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$)	K_m (μM)
(Per)chlorate reductase	Perchlorate	7.3	62
(Per)chlorate reductase	Chlorate	13.2	4
Chlorite dismutase	Chlorite	2,200	170

Applications of (per)chlorate-utilizing microorganisms

Removal of chlorate from wastewater

The capacity to reduce (per)chlorate is distributed among hydrogen gas oxidizers (van Ginkel *et al.* 1995). The use of hydrogen gas as electron donor in biological wastewater treatment offers major benefits, such as process reliability and no need for removal of residual reductant (Kurt *et al.* 1987, van Houten *et al.* 1994). Because of the low water solubility of hydrogen, efficient mass transfer from the gas to liquid phase as achieved in gas-lift reactors is essential.

A model wastewater containing 0.5 g/L of chlorate was used to assess the performance of a gas-lift bioreactor. Complete chlorate reduction and the concomitant formation of chloride was observed after 2 weeks of operation with activated sludge as inoculum. A stepwise decrease in HRT down to 6 hours did not show any decrease in degradation efficiency (Figure 2). A further decrease in HRT to 3 hours resulted in a decline in chlorate reduction. After 2 months of operation biomass, formation on the outside of the pumice particles became clearly visible by light microscopy. After vigorously shaking for several hours the biofilm did not disintegrate, indicating that a stable biofilm had developed.

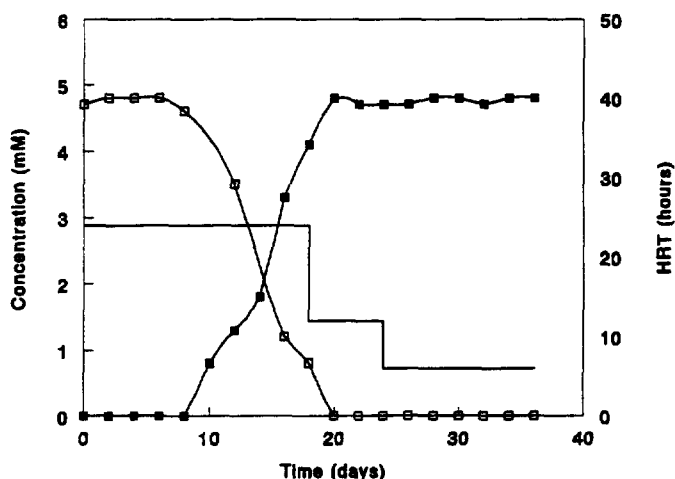


Figure 2
Reduction of chlorate (□) to chloride (■) in a gas-lift bioreactor during start-up at an HRT 24 hours. After 20 days of operation the HRT (-) was decreased stepwise down to 6 hours.

The reduction of chlorate by immobilized microorganisms was coupled to the oxidation of hydrogen gas, whereas chlorite reduction was not affected by hydrogen gas. The immobilized microorganisms also disproportionate chlorite into molecular oxygen and chloride. As a consequence the immobilized microorganisms oxidized hydrogen by simultaneously reducing chlorate to chlorite and oxygen to water.

Removal of perchlorate and chlorite from drinking water

A reactor packed with pumice particles collected from the gas-lift bioreactor mentioned above was used to evaluate the removal of chloro-oxo acids from potable water. Experiments were undertaken by running this bioreactor at an influent concentration of 2 mg/L perchlorate and chlorate. Over 99 per cent of the perchlorate and chlorate was reduced to chloride in the reactor at HRTs of 120 and 8 minutes, respectively. Figure 3 shows the influence of the HRT on the degree of reduction of chlorite. Reduction of these chloro-oxo acids was achieved under anaerobic conditions with hydrogen gas saturated water. The nontoxicity and low water solubility of hydrogen makes it a safe and reliable reductant for a process to remove perchlorate from drinking water (Kurt *et al.* 1986). Removal of chlorite does not require a reducing agent. Immobilized chlorate-utilizing microorganisms in the packed column were fed with deionized water containing 2.0 mg/L chlorite. In the packed bed the chlorite content of the water was reduced to < 0.1 mg/L. Complete removal of chlorite from water was attained at a HRT of 0.2 minute. Maximum conversion rates of 720 g chlorite.m⁻³ reactor.hour⁻¹, 30 g chlorate.m⁻³ reactor.hour⁻¹ and 1 g perchlorate.m⁻³ reactor.hour⁻¹ determined in the packed bed reactor reflect activities of chloro-oxo acids in strain GR-1 (Table I).

Conclusions

Bacteria are capable of reducing perchlorate and chlorate to chloride under anaerobic conditions with electron donors such as hydrogen gas and acetate. Chlorite is disproportionated under aerobic conditions by (per)chlorate-grown cells. Efficient rates of reduction of these chloro-oxo acids at both low and high concentrations were achieved in a packed column and a gas-lift bioreactor, respectively, with hydrogen gas as reducing agent. The use of immobilized (per)chlorate-utilizing microorganisms is therefore a feasible approach to remove chloro-oxo acids present in wastewater and drinking water

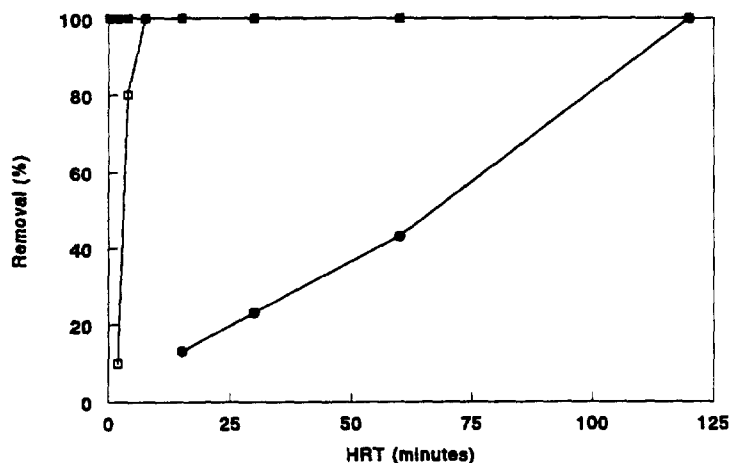


Figure 3
Removal of perchlorate (●), chlorate (○) and chlorite (■) present at 2 mg/L in deionized water in a packed bed reactor at various HRTs.

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Public Health Goals for California Drinking Water: Methyl Tertiary Butyl Ether (MTBE) and Perchlorate.

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The office of Environmental Health Hazard Assessment (OEHHHA) of the California Environmental Protection Agency has the chief responsibility for conducting human health risk assessment and developing risk assessment methodology as applied to chemical pollutants in the environment. OEHHHA has been involved with MTBE for a number of years and in 1991 adopted a drinking water interim Action Level of 35 ppb (ug/L). While OEHHHA was updating this earlier Action Level, recent California legislation, particularly SB512 and SB 1189 of 1997, gave OEHHHA a mandate to develop a public health goal (PHG) for MTBE. PHG values are advisory and like Action Levels are based solely on health based criteria, but PHGs also serve as a prelude to primary state drinking water standards or maximum contaminant levels (MCLs). The California Department of Health Services (CDHS) uses the PHG and other technical and economic factors in setting the MCL. At present OEHHHA is preparing a draft risk assessment document for MTBE in drinking water (OEHHHA, 1998). The draft risk assessment evaluates both carcinogenic and noncarcinogenic endpoints. Exposure to MTBE from non-water sources, such as ambient air, as well as non-ingestion routes, such as showering, are also accounted for in the assessment. Further revisions based on comments from the public and other government agencies are expected before the PHG is adopted and the technical support document finalized. It is anticipated that the PHG for MTBE will be adopted during the third quarter of 1998.

Perchlorate contamination of groundwater has been observed in a number of areas near facilities that use solid rocket propellants, notably in Rancho Cordova near Sacramento, CA. Recently introduced legislation (SB1033, Sher) would require OEHHHA to adopt a PHG for perchlorate over a short period of time similar to the MTBE mandate noted above. In 1997 the CDHS requested that OEHHHA provide an evaluation of current data that would support a provisional Action Level for perchlorate in drinking water. OEHHHA's evaluation relied heavily on one conducted by U.S. EPA (1995) which identified a range of "safe" drinking water concentrations from 4 ppb to 18 ppb based on an oral reference dose (RfD) range of 1E-4 to 5E-4 mg/kg-d. OEHHHA staff calculated a value of 17.5 ppb based on the 5E-4 mg/kg-d RfD for an adult consuming 2L of water per day, and recommended a provisional action level of 18 ppb (OEHHHA, 1997). There are still several data gaps in perchlorate toxicology and new studies are presently being conducted to address many of these. Sensitive subgroups would likely include children, people on low iodine diets or deficient in iodine uptake, and people with hypothyroidism. Perchlorate is a recognized anti-thyroid agent and endocrine disrupter according to U.S. EPA's recent guidance (U.S. EPA, 1997).

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